Inorganic Polymers, Second Edition

James E. Mark
Harry R. Allcock
Robert West

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Preface to the Second Edition

As was the case with the first edition, the goal was to provide a broad overview of inorganic polymers in a way that will be useful to both the uninitiated and to those already working in this field. The coverage has been updated and expanded significantly to cover advances and interesting trends since the first edition appeared. The most obvious changes are the three new chapters, “Ferrocene-Based Polymers, and Additional Phosphorus- and Boron-Containing Polymers,” “Inorganic-Organic Hybrid Composites,” and “Preceramic Inorganic Polymers.”

The authors once again hope that readers will be inspired to enter and contribute to this fascinating area of inorganic polymeric materials.

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Preface to the First Edition

Most polymers being synthesized, characterized, and utilized in today's world are organic in nature. That is, their chain backbones consist primarily of carbon atoms, frequently along with some heteroatoms such as oxygen and nitrogen. Their attractive properties, such as easy processibility, high strength, and low density, have been exploited in all industrialized societies to the extent that it is now difficult to imagine life without them.

In spite of their many successes, organic polymers have a number of deficiencies. For one, the monomers from which they are prepared are frequently subject to the vagaries of the petroleum industry. The polymers themselves frequently have low softening temperatures or low degradation temperatures. Many are also vulnerable to degradation from oxygen, ozone, or high-energy radiation. Some are subject to dissolution or swelling when in contact with solvents or fluids in commercial applications. Finally, many present environmental problems by resisting incorporation into the biosphere, or by forming highly toxic products upon combustion.

Inorganic polymers, with backbones typically of silicon, phosphorus, oxygen, or nitrogen atoms, are now being more and more intensively studied. One obvious reason is the quest to find materials not suffering from some of the limitations mentioned above. No single polymer, of course, can be expected to meet all of the desired properties for an application, particularly in the high-technology area. Nonetheless, the very different chemical nature of inorganic materials suggests they could well be superior to their organic counterparts in a variety of ways. The polysiloxanes, with their superb thermal stability, are a good example in this regard. The controlled degradability and the innocuous degradation products of polyphosphazenes in controlled drug-delivery systems is another.

There are numerous other reasons for being interested in inorganic polymers. One is the simple need to know how structure affects the properties of a polymer, particularly

outside the well-plowed area of organic materials. Another is the bridge that inorganic polymers provide between polymer science and ceramics. More and more chemistry is being used in the preparation of ceramics of carefully controlled structure, and inorganic polymers are increasingly important precursor materials in such approaches.

The present book was prepared to provide an introduction to the field of inorganic polymers. There has long been a need for such a book, as opposed to the ready availability of numerous other books, that are highly specialized and written for scientists already working in this area. The only background required for its comprehension are the basic concepts presented in a typical undergraduate course in chemistry. Some familiarty with the fundamentals of polymer science would be helpful, but not necessary, since many of these are covered in an introductory chapter on polymer characterization.

It is hoped that the book will be useful to a variety of readers, including polymer chemists, inorganic chemists, chemical engineers, and materials scientists. The highly tutorial nature of the presentation should also make it useful as a textbook, for a one-term course.

One of the advantages of writing a book is the uncovering of an almost endless series of interesting research ideas. We hope our readers benefit in the same way and will explore more deeply this fascinating new area of polymer science and engineering.

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About the Authors

James E. Mark received his B.S. degree in 1957 in Chemistry from Wilkes College and his Ph.D. degree in 1962 in Physical Chemistry from the University of Pennsylvania. After serving as a Postdoctoral Fellow at Stanford University under Professor Paul J. Flory, he was Assistant Professor of Chemistry at the Polytechnic Institute of Brooklyn before moving to the University of Michigan, where he became a Full Professor in 1972. In 1977, he assumed the position of Professor of Chemistry at the University of Cincinnati, and served as Chairman of the Physical Chemistry Division and Director of the Polymer Research Center. In 1987, he was named the first Distinguished Research Professor, a position he holds at the present time. In addition, he has extensive research and consulting experience in industry and has served as a Visiting Professor at several institutions. Dr. Mark's research interests pertain to the physical chemistry of polymers, including the elasticity of polymer networks, hybrid organic-inorganic composites, liquid-crystalline polymers, and a variety of computer simulations. Dr. Mark is an extensive lecturer in polymer chemistry, is an organizer and participant in a number of short courses, and has published approximately 625 research papers and coauthored or coedited twenty books. He is the founding editor of the journal *Computational and Theoretical Polymer Science*, which was started in 1990, is an editor for the journal *Polymer,* and serves on a number of journal Editorial Boards. He is a Fellow of the New York Academy of Sciences, the American Physical Society, and the American Association for the Advancement of Science. His awards include the Dean's Award for Distinguished Scholarship, the Rieveschl Research Award, and the Jaffe Chemistry Faculty Excellence Award (all from the University of Cincinnati), the Whitby Award and the Charles Goodyear Medal (Rubber Division of the American Chemical Society), the ACS Applied Polymer Science Award, the Flory Polymer Education Award (ACS Division of Polymer Chemistry), election to the Inaugural Group of Fellows (ACS Division of Polymeric Materials Science and Engineering),

the Turner Alfrey Visiting Professorship, the Edward W. Morley Award from the ACS Cleveland Section, the ACS Kipping Award in Silicon Chemistry, the Reed Lectureship at Rensselaer, and an Award for Outstanding Achievement in Polymer Science and Technology from the Society of Polymer Science, Japan.

Harry Allcock has devoted most of his career to the field of inorganic polymers. He was responsible for the design and synthesis of the first stable polyphosphazenes, and he and his coworkers at The Pennsylvania State University have played a major role in the development of this field through their 475 research publications. His research focuses on fundamental synthetic chemistry and an understanding of structure–property relationships, together with explorations of possible applications for the new polymers in biomedicine, aerospace, energy storage and generation, and communications technology. Allcock has also written three monographs on inorganic rings and macromolecules, has coauthored a widely used textbook on polymer chemistry and an introductory text on inorganic polymers, and has coedited three books on inorganic chemistry and inorganic materials. He is the recipient of three American Chemical Society National Awards, is a Guggenheim Fellow, and has lectured widely on polyphosphazenes and other inorganic polymer systems. Allcock was born and educated in the United Kingdom and received B.Sc. and Ph.D. degrees from the University of London. His position as an Evan Pugh Professor of Chemistry at Penn State is the highest academic honor bestowed by the University.

Robert West was born in New Jersey and educated at Cornell University (B.A.) and Harvard University (A.M., Ph.D.). For the past 45 years he has been a faculty member in the chemistry department at the University of Wisconsin, where he is now E. G. Rochow Professor and Director of the Organosilicon Research Center. His many awards include the Frederick Stanley Kipping Award, the Wacker silicone prize, the Alexander von Humboldt Award, and the main group chemistry medal. He has published more than 600 scientific papers, mostly in the area of silicon chemistry. Major discoveries in his laboratories include the first soluble polysilanes (1978), the silicon-silicon double bond (1981), the first stable silylenes (1994), and electrically conducting organosilanes for high energy density batteries (2000). He is an airplane pilot and a mountaineer, with numerous first ascents in Canada and Alaska.

INORGANIC POLYMERS

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1

Introduction

1.1 What Is a Polymer?

A polymer is a very-long-chain macromolecule in which hundreds or thousands of atoms are linked together to form a one-dimensional array. The skeletal atoms usually bear *side groups*, often two in number, which can be as small as hydrogen, chlorine, or fluorine atoms or as large as aryl or long-chain alkyl units. Polymers are different from other molecules because the long-chain character allows the chains to become entangled in solution or in the solid state or, for specific macromolecular structures, to become lined up in regular arrays in the solid state. These molecular characteristics give rise to solid-state materials properties, such as strength, elasticity, fiber-forming qualities, or film-forming properties, that are not found for small molecule systems. The molecular weights of polymers are normally so high that, for all practical purposes, they are nonvolatile. These characteristics underlie the widespread use of polymers in all aspects of modern technology. Attempts to understand the relationship between the macromolecular structure and the unusual properties characterize much of the fundamental science in this field.

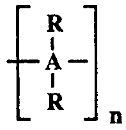
1.2 How Polymers Are Depicted

Polymers are among the most complicated molecules known. They may contain thousands of atoms in the main chain, plus complex clusters of atoms that form the side groups attached to the skeletal units. How, then, can we depict such molecules in a manner that is easy to comprehend?

First, an enormous simplification can be achieved if we remember that most synthetic polymers contain a fairly simple structure that repeats over and over down the chain. This simplest repetitive structure is known as the *repeating unit*, and it provides the basis for an uncomplicated representation of the structure of the whole polymer.

For example, suppose that a polymer consists of a long chain of atoms of type A, to which are attached side groups, R. The polymer chain can be represented by the formula shown in **1.1**. The two horizontal lines represent the bonds of the main chain. The brackets (or parentheses) indicate that the structure repeats many times. The actual number of repeating units present is normally not specified, but is represented by the subscript, *n*. If only a few repeating units (for example, 5–20) are present, *n* is usually replaced by *x*. Note that this formula says nothing about end groups that may be present. If the polymer chain is very long, the end groups represent only a small component of the molecule, and are ignored in the formula. The formula shown in **1.1** can also represent a cyclic (or macrocyclic) structure in which, of course, no end groups are present.

When the repeating unit contains two or more different skeletal elements, the formula can be expanded as shown in **1.2**. If different repeating units bear different side groups (R and X), a formula such as **1.3** may be used. However, beyond a certain point, the complexity of the molecule cannot be represented by a simple formula. For example, **1.4** tells us nothing about whether the R groups on adjacent repeating units are *cis*- or *trans*- to each other. Such information is usually best described by supporting information in the text rather than by adding to the complexity of the formula.



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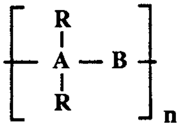

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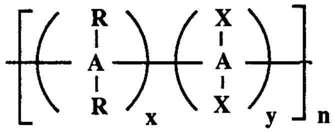

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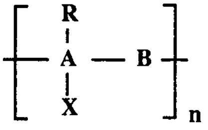

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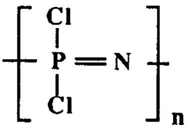

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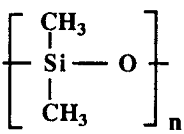

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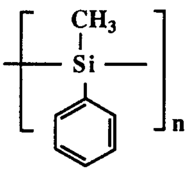

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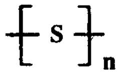

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The *naming* of polymers in this book follows an accepted practice used by the vast majority of polymer chemists (though not by specialists in nomenclature). In the system used here, the name of the repeating unit is preceded by the word “poly.” If parentheses or brackets are needed to avoid ambiguity, they are used. If not needed, they are left out. For example, Polymer **1.5** is named poly(dichlorophosphazene), Species **1.6** is called poly(dimethylsiloxane), and Polymer **1.7** is poly(methylphenylsilane). Species **1.8** is polysulfur.

1.3 Reasons for Interest in Inorganic Polymers

Polymer chemistry and technology form one of the major areas of molecular and materials science. This field impinges on nearly every aspect of modern life, from electronics technology, to medicine, to the wide range of fibers, films, elastomers, and structural materials on which everyone depends.

Most of these polymers are organic materials. By this we mean that their long-chain backbones consist mainly of carbon atoms linked together or separated by heteroatoms such as oxygen or nitrogen. Organic polymers are derived either from petroleum or (less frequently) from plants, animals, or microorganisms. Hence, they are generally accessible in large quantities and at moderate cost. It is difficult to imagine life without them.

In spite of the widespread importance of organic polymers, attention is being focused increasingly toward polymers that contain inorganic elements as well as organic components. At the present time, most of this effort is concentrated on the development of new *chemistry*, as research workers probe the possibilities and the limits to the synthesis of these new macromolecules and materials. But in certain fields, particularly for polysiloxanes, both the science and the technology are already well established, and technological developments now account for a major part of the siloxane literature. For other systems to be discussed in this book, technological developments are emerging from the chemistry at an accelerating rate.

Why, with the hundreds of organic polymers already available, should scientists be interested in the synthesis of even more macromolecules? The reasons fall into two categories. First, most of the known organic polymers represent a compromise in properties compared with the “ideal” materials sought by engineers and medical researchers. For example, many organic backbone polymers react with oxygen or ozone over a long period of time and lose their advantageous properties. Most organic polymers burn, often with the release of toxic smoke. Many polymers degrade when exposed to ultraviolet or gamma radiation. Organic polymers sometimes soften at unacceptably low temperatures, or they swell or dissolve in organic solvents, oils, or hydraulic fluids. At the environmental level, few organic polymers degrade at an acceptable rate in the biosphere. Finally, the suspicion exists that the availability of many organic polymers may one day be limited by the anticipated scarcities of petroleum. It is generally accepted that polymers that contain inorganic elements in the molecular structure may avoid some or all of these problems.

The second set of reasons for the burgeoning interest in inorganic-based macromolecules is connected with their known or anticipated *differences* from their totally organic counterparts. Inorganic elements generate different combinations of properties in polymers

than do carbon atoms. For one thing, the bonds formed between inorganic elements are often longer, stronger, and more resistant to free radical cleavage reactions than are bonds formed by carbon. Thus, the incorporation of inorganic elements into the backbone of a polymer can change the bond angles and bond torsional mobility, and this in turn can change the materials properties to a remarkable degree. Inorganic elements can have different valencies than carbon, and this means that the number of side groups attached to a skeletal atom may be different from the situation in an organic polymer. This will affect the flexibility of the macromolecule, its ability to react with chemical reagents, its stability at high temperatures, and its interactions with solvents and with other polymer molecules. Moreover, the use of non-carbon elements in the backbone provides opportunities for tailoring the chemistry in ways that are not possible in totally organic macromolecules. Many examples of this feature are given in the later chapters of this book. Thus, the future development of polymer chemistry and polymer engineering may well depend on the inorganic aspects of the field for the introduction of new molecular structures, new combinations of properties, and new insights into the behavior of macromolecules in solution and in the solid state.

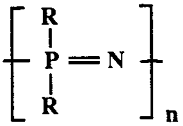
Thus, inorganic polymers provide an opportunity for an expansion of fundamental knowledge and, at the same time, for the development of new materials that will assist in the advancement of technology. Throughout this book an attempt has been made to connect these two aspects in a way that will provide a perspective of this field. For example, the superb thermal stability of several poly(organosiloxanes) can be understood in terms of their fundamental chemistry. The controlled hydrolytic degradability of certain polyphosphazenes, which depends on molecular design to favor specific hydrolysis mechanisms, is the basis for their prospective use as pharmaceutical drug delivery systems. The unusual energy absorption characteristics of polysilanes is indicative of surprising electronic structures, and this underlies the interest in some of these materials for use in integrated circuit fabrication.

1.4 Types of Inorganic Polymers

A glance at the Periodic Table or at an inorganic chemistry textbook will convince the reader that, of the 100 or so stable elements in the table, at least half have a chemistry that could allow their incorporation into macromolecular structures. This will undoubtedly come to pass in the years ahead. However, at the present time, most of the known inorganic polymer systems are based on relatively few elements that fall within the region of the Periodic Table known as the "Main Group" series. These elements occupy groups III (13 in the IUPAC nomenclature), IV (14), V (15), and VI (16) and include elements such as silicon, germanium, tin, phosphorus, and sulfur. Of these, polymers based on the elements silicon and phosphorus have received by far the most attention. This is the reason why silicon- and phosphorus-containing polymers are considered in the greatest detail in this book.

Specifically, the greatest emphasis in the following chapters is placed on polyphosphazenes (**1.9**), polysiloxanes (**1.10**), and polysilanes (**1.11**). Chapters 6 and 7 introduce a wide variety of other polymers that contain elements such as phosphorus, germanium, sulfur, boron, aluminum, and tin, and a variety of transition metals. These polymers are expected to provide the basis for many of the new advances of the future. Chapter 8

deals with inorganic polymers that have been incorporated into composites, and Chapter 9 describes how inorganic polymers are used as precursors to ceramics.



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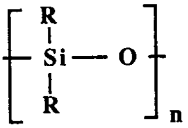

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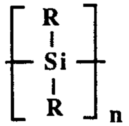

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1.5 Special Characteristics of Polymers

Polymer molecules have many special characteristics that may be unfamiliar to some readers of this book. For this reason, the following chapter has been devoted to a summary of the special techniques used for the characterization and study of macromolecules. The remaining chapters deal with the synthesis, reaction chemistry, molecular structural, and applied aspects of selected inorganic polymer systems.

2

Characterization of Inorganic Polymers

2.1 Molecular Weights

2.1.1 Introduction

Importance

A wide variety of properties are of interest for the general characterization of polymers, as demonstrated in numerous textbooks[1–16] and in more specialized books dealing specifically with characterization methods.[17–22] In addition to the information of this type appearing in this chapter, there is related information in numerous other parts of this book, in particular in Chapters 4 and 8. From any of these sources of information, it becomes immediately obvious that one of the most important properties of a polymer molecule is its molecular weight. This is the characteristic that underlies all the properties that distinguish a polymer from its low-molecular-weight analogues. Thus, one of the most important goals in the preparation of a polymer is to control its molecular weight by a suitable choice of polymerization conditions.

Many properties of a polymeric material are improved when the polymer chains are sufficiently long. For example, properties such as the tensile strength of a fiber, the tear strength of a film, or the hardness of a molded object may increase asymptotically with increases in molecular weight, as is shown schematically in Figure 2.1. If the molecular weight is too low, say below a lower limit M_l, then the physical property could be unacceptably low. It might also be unacceptable to let the molecular weight become too high. Above an upper limit M_u, the viscosity of the bulk (undiluted) polymer might be too high for it to be processed easily. Thus, a goal in polymer synthetics is to prepare a polymer so that its molecular weight falls within the "window" demarcated by M_l and M_u. This is frequently accomplished by a choice of reaction time, temperature, nature and amount of catalyst, the nature and amount of solvent, the addition of reactants that

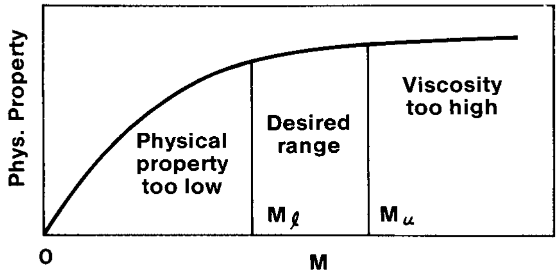


Figure 2.1 Typical dependence of a physical property on the molecular weight of a polymer. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

can terminate the growth of the polymer chains sooner than would otherwise be the case, addition of complexing agents such as crown ethers, or by the presence of an external physical field, such as ultrasound.

Statistical Aspects

The termination of the growth of a particular chain molecule is a statistical process. If termination happens soon after the chain starts to grow then, obviously, the completed chain will be short. If the chain evades termination for a while, it will be longer. Because of this, polymers are usually characterized by a *distribution* of molecular weights. This distinguishes them from their low-molecular-weight analogues, and causes any experimentally determined molecular weight to be an average. Such an average molecular weight is generally determined by dissolving the polymer in a solvent, followed by measurement of some physical property of the resultant solution. An additional complication arises from the fact that different properties can depend on molecular weight in very different ways. Because of this, it is necessary to define the different types of averages, since these emphasize different ranges of the molecular weight distribution.

2.1.2 Types of Molecular Weights

The first type of molecular weight is the *number-average*, and is defined by

$$M_n = \frac{\sum N_i M_i}{\sum N_i} \tag{1}$$

where N_i is the number of molecules that have a molecular weight M_i. This type of average is also called the "mean" value of a distribution. (The same types of summations are carried out in calculating the average grade in an examination, wherein five students who score 90 points each would contribute 5 × 90 points to the numerator, and five events to the denominator, etc.) This type of average is obtained by use of any technique that "counts" particles, for example

- end-group analysis
- vapor-pressure lowering
- boiling-point elevation

- melting-point depression
- osmotic pressure

These are the so-called "colligative" properties, where the adjective signifies a "tying together" of all properties that have a particular characteristic. Specifically, they depend only on the *number* (molar) concentration of particles present.

The *weight-average* molecular weight is defined by

$$\mathrm{M_w} = \frac{\sum N_i M_i^2}{\sum N_i M_i} \tag{2}$$

in which the N_i weighting factor that appears in equation (1) has been replaced by N_iM_i, which is proportional to the *weight* of polymer that has the specified M_i. A measurement of the intensity *i* of light scattered from a polymer chain in solution is the most common way to obtain this type of average, and it depends on the fact that *i* is proportional to the *square* of the molecular weight of the polymer chain that is the origin of the scattering.

These two types of molecular weight averages are representative of the type called "absolute" methods, in that well-established thermodynamic equations can be used to convert the experimental data directly into a value of the molecular weight. However, some other methods require calibration. The most important of these "indirect" methods involves a measurement of the intrinsic viscosity. This quantity is a measure of the extent to which a polymer molecule increases the viscosity of the solvent in which it is dissolved. The viscosity method can be calibrated to yield a viscosity-average molecular weight, defined by

$$M_\mathrm{v} = \left[\frac{\sum N_i M_i^{1+a}}{\sum N_i M_i}\right]^{1/a} \tag{3}$$

A solution viscosity measurement is a hydrodynamic-thermodynamic technique, and the extent to which a polymer molecule increases the viscosity of a solvent depends on the nature of its interactions with that solvent (as well as on its own molecular weight). These interactions are characterized by the quantity *a* that appears in equation (3). The calibration of the method, using samples, of the same polymer having known molecular weights, in essence determines its value. The disadvantage of this calibration requirement is offset by the simplicity of the experimental measurements.

2.1.3 Experimental Techniques

Colligative Properties

A *chemical* method for determining number-average molecular weights involves an analysis of end groups. If the polymer was prepared in such a way that each chain has either one or two labelled ends, then analysis for these ends is equivalent to counting the chains. For example, the ends could be hydroxyl groups or radioactive initiator fragments, and the analysis could involve titration, spectroscopy, or measurements of radioactivity. Chains formed in condensation polymerizations, from A-B monomers

for example, automatically have A and B functional groups at their ends.[15,23] The number of chains gives the number of moles of chains, and the weight of the sample divided by the number of moles gives the desired molecular weight. The method works best for relatively low molecular weights (below about 25,000) where the number-density of chain ends is not too small.

Vapor-pressure lowering, boiling-point elevation, and freezing-point depression are very similar thermodynamically. For example, the increase in boiling point ΔT_b is interpreted thermodynamically by using the boiling-point elevation constant K_b to obtain the molality of the solution, as stated in the equation

$$\Delta T_b = K_b m \tag{4}$$

where m is the molality. The weight concentration c of the same solution is, of course, known from the weights of its components. The factor that converts the molar concentration to the weight concentration is simply the desired molecular weight. This is shown in the equation

$$m(\text{moles/kg solvent})\ M(\text{g/mole}) = c(\text{g/kg solvent}) \tag{5}$$

These methods also become less reliable as the molecular weight increases because fewer solute particles are now present in the system.

The final colligative property, osmotic pressure,[24–29] is different from the others and is illustrated in Figure 2.2. In the case of vapor-pressure lowering and boiling-point elevation, a natural boundary separates the liquid and gas phases that are in equilibrium. A similar boundary exists between the solid and liquid phases in equilibrium with each other in melting-point-depression measurements. However, to establish a similar equilibrium between a solution and the pure solvent requires their separation by a semipermeable membrane, as illustrated in the figure. Such membranes, typically cellulosic, permit transport of solvent but not solute. Furthermore, the flow of solvent is from the solvent compartment into the solution compartment. The simplest explanation of this is the increased entropy or disorder that accompanies the mixing of the transported solvent molecules with the polymer on the solution side of the membrane. Flow of liquid up the capillary on the left causes the solution to be at a hydrostatic pressure

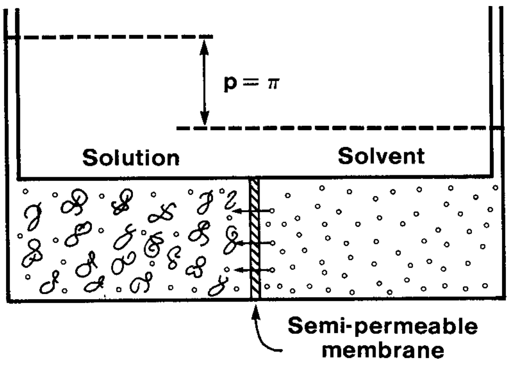


Figure 2.2 Schematic diagram of a membrane osmometer. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

that is higher than that on the solvent side. The back pressure that is just sufficient to prevent further transport of solvent through the membrane is called the osmotic pressure π of that solution.

For an ideal solution (one that obeys Raoult's law)[30,31]

$$\pi = RTm' \tag{6}$$

where m' is the molarity (moles/cc of soln). Also, in parallel with equation (5),

$$m'M = c' \tag{7}$$

and thus $\pi = cRT/M$, which is analogous to the ideal gas law, $p = nRT/V = cRT/M$.

Since polymer solutions are markedly non-ideal, osmotic pressure data are taken at low concentrations and are extrapolated to infinite dilution $(c \rightarrow 0)$. In the case of membrane osmometry, the relevant equation is

$$\begin{aligned} \pi/cRT &= 1/M + A_2C + A_3C^2 + \cdots \\ &\cong 1/M + A_2C \end{aligned} \tag{8}$$

where the second virial coefficient A_2 provides a measure of the polymer–solvent interactions. The larger its value, the stronger are these interactions, and the more non-ideal is the solution. Some typical results are shown schematically in Figure 2.3.

In membrane osmometry, molecular weights above a million are essentially impossible to measure because there are too few particles in a given weight of polymer. On the other hand, polymers with molecular weights less than 25,000 can cause problems by themselves diffusing through the membrane.

A related technique, vapor phase osmometry, is based on the idea of "isothermal distillation." Such an osmometer is shown schematically in Figure 2.4. In effect, the vapor

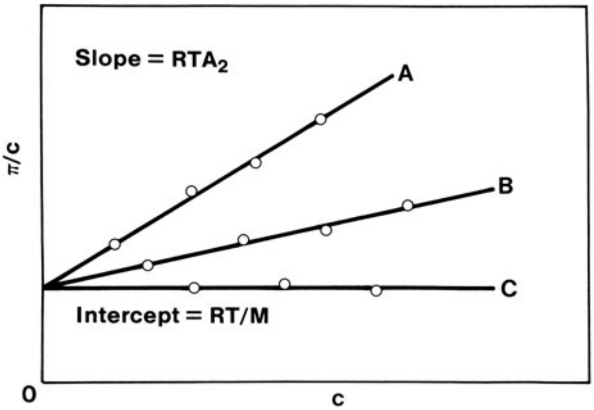


Figure 2.3 Typical osmotic pressure data, where solvent A is a very good solvent (strong polymer-solvent interactions), B is a moderately good solvent, and C is a Θ solvent (in which polymer-solvent interactions have been adjusted to nullify the excluded volume effect).[31a] Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

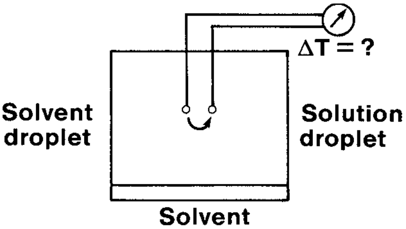


Figure 2.4 Schematic diagram of a vapor phase osmometer. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

phase replaces the membrane in membrane osmometry. Thus, it permits passage of the solvent but not the polymer. A droplet of solvent is placed on one thermistor, and a droplet of solution on another thermistor. The solvent molecules can vaporize and do so preferentially from the pure solvent droplet. The different rates of evaporation generate different temperatures, and the difference in temperature ΔT between the two droplets is measured.

A problem with the technique is that, because of thermal losses, the temperature never really stabilizes and a thermodynamic analysis can not be applied. It is customary, therefore, simply to take the relatively constant value of ΔT that appears near the maximum in a plot of ΔT against time.

This is not an absolute method, and it has to be calibrated. A plot is made of temperature difference against molar concentration, using a relatively low-molecular-weight solute of high purity and known molecular weight. Once the calibration curve has been established, any measured value of ΔT can be converted to a molar concentration, and thus a molecular weight can be obtained, using an equation such as (5) or (7).

The molecular weight of the solute should be small, but not so small as to allow it to be volatile.

Light Scattering

A typical photometer used in light scattering measurements is shown in Figure 2.5. The symbol S locates the source of the light (often a laser), F represents filters which are sometimes needed for making the radiation more nearly monochromatic or decreasing its intensity, L is a collimating lens, C is the sample cell, T is a trap for the non-scattered incident beam, and PH is the photocell for measuring the intensity of the scattered radiation.

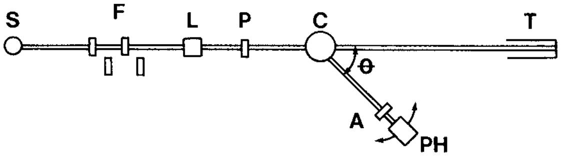


Figure 2.5 Sketch of the major components of a light scattering photometer. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

The photocell is mounted on a turntable so that intensities can be measured as a function of scattering angle θ as well as concentration. P and A are a polarizer and an analyzer, respectively, and can be used to measure the optical anisotropy of the polymer.[15]

The quantity of primary interest is the "Rayleigh" ratio, which is defined by

$$R''_\theta = i_\theta r^2/I_0 \tag{9}$$

where i_θ is the intensity of scattered beam, I_0 the intensity of incident beam, and r the distance from detector to scattering cell. The ratio i_θ/I_0 is in the vicinity of 10^{-5}, which can complicate designing a photometer of this type. The Rayleigh ratio also contains r^2, the square of the distance between the detector and the scattering cell. Since the intensity of light decreases inversely with the square of distance, this makes the Rayleigh ratio independent of this arbitrary design feature.

Two corrections are required to the Rayleigh ratio as defined by equation (9). Because the solvent, as well as the polymer, scatters the radiation, and only the polymer contribution is of interest, each value of the Rayleigh ratio must be corrected as shown by the equation

$$R'_\theta = R''_\theta(\text{soln}) - R''_\theta(\text{solvent}) \tag{10}$$

An additional factor, sin θ, is required to correct for the increase in scattering volume that occurs with changes in scattering angle away from the reference value of 90°. A final factor $1/(1 + \cos^2 \theta)$ is required to take into account the fact that the horizontal and vertical components of light are scattered to different extents. These final two corrections are incorporated in the equation

$$R_\theta = R'_\theta\left[\sin\theta/\left(1+\cos^2\theta\right)\right] \tag{11}$$

The scattering function Kc/R_θ is the quantity directly related to the physical properties of interest. It consists of an optical constant K times the concentration, divided by the Rayleigh ratio. The constant K is defined by

$$K = \left(2\pi^2 n_0^2/N_{\text{avo}}\lambda^4\right)\left(\text{d}n/\text{d}c\right)^2 \tag{12}$$

and consists of the numerical constant $\pi = 3.14159\ldots$, the index of refraction of the pure solvent n_0, Avogadro's number, the wave length λ of the light, and the dependence of the index of refraction of the solution on concentration.

There are two uses of the scattering function. If its value at zero scattering angle is plotted against concentration, then the intercept is the reciprocal of the molecular weight of the polymer, and the slope of the line is twice the second virial coefficient. The relevant equation is

$$\left(Kc/R_\theta\right)_{\theta\to 0} = 1/M + 2A_2c + \cdots \tag{13}$$

In addition, if the scattering function at zero concentration is plotted against $\sin^2(\theta/2)$, then the intercept gives a check on the molecular weight, and the slope gives the radius of gyration $\langle s^2 \rangle$. The detailed mathematical relationship is given by

$$\left(Kc/R_\theta\right)_{c\to 0} = (1/M)\left[1+\left(16\pi^2/3(\lambda/n_0)^2\right)\left\langle s^2\right\rangle \sin^2(\theta/2)+\cdots\right] \quad (14)$$

In interpreting the light scattering from a polymer solution, the required extrapolations to zero scattering angle and zero concentration are usually carried out simultaneously. The result is called a Zimm plot and is described in Figure 2.6. The scattering function is plotted as the ordinate and the abscissa is a composite quantity: $\sin^2(\theta/2)$ + a constant (100) times the concentration. The constant is arbitrary and merely determines how spread out the data will be.

The open circles in the uppermost line in Figure 2.6 locate data taken at the highest concentration. These data are extrapolated over to give the point that corresponds to zero scattering angle at this concentration. Since at $\theta = 0°$, $\sin^2(\theta/2) = 0$, the abscissa of the desired point, located by the filled circle, is simply 100 times the constant value of the concentration. This is repeated for the other (essentially parallel) constant concentration lines to give the other points that correspond to zero angle. These points are then extrapolated to give an intercept that yields the molecular weight. The slope gives the second virial coefficient.

The more nearly vertical lines in the grid correspond to fixed scattering angle, with the line furthest to the right corresponding to the widest angle. Each such line is extrapolated downward to give the point that corresponds to zero concentration at this fixed value of θ. At $c = 0$ the abscissa of the desired point is simply sin-squared of half that particular angle. In this way, the location of each of the filled triangular points

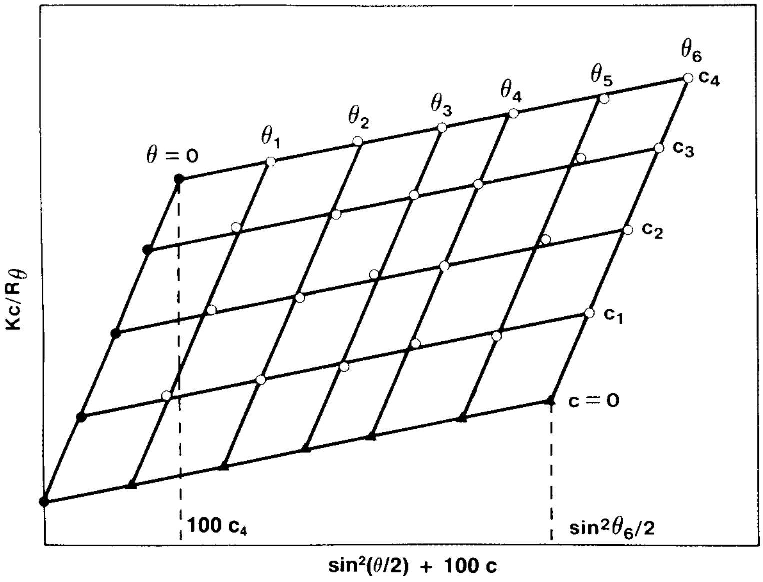


Figure 2.6 A Zimm plot, in which light-scattering data are simultaneously extrapolated to zero-scattering angle and zero concentration. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

is determined. They are themselves then extrapolated to give the intercept, and to yield a check of the molecular weight. The slope gives the mean-square radius of gyration.

A Zimm plot does simultaneously what is described in equations (13) and (14). There is an advantage in being able to find the intercept that is most consistent with both the concentration dependence and the angular dependence.

Advantages of the light-scattering technique include the wide range of molecular weights that can be determined, and the ability to measure dimensions of the polymer coil in solution and to study the interactions between the polymer and solvent in the solution. The main disadvantages are the absolutely critical need to remove all dust particles (which scatter tremendously because their effective molecular weights are extraordinarily high), and the complexity of the equipment. Recent advances in instrumentation include the use of lasers, and the replacement of a single photocell (which had to be rotated on a platter to obtain scattering intensities as a function of angle θ) by an array of photocells located at fixed angles.[15] This approach permits the simultaneous gathering of the scattering intensities at the various values of θ. It also minimizes errors in the angular settings, and facilitates the use of software programs for calculations of molecular weights, second virial coefficients, and radii of gyration.

Viscometry

This technique is by far the easiest for the characterization of polymers in solution. This can be seen from the simplicity of the typical (glass) viscometer shown in Figure 2.7. It is used to obtain the viscosity of a liquid by the use of Poiseuille's equation, which is

$$\eta = \pi p r^4 t / 8LV \tag{15}$$

The experiment involves a measurement of the amount of time t required for a volume V of liquid to flow through a capillary of radius r and length L when the pressure difference is p. The viscosity η may then simply be calculated from this equation, in which the π is the numerical constant.

In polymer solution viscometry, it is not necessary to determine absolute values of the viscosity; relative values are sufficient. These quantities are called "viscosities," but the terms are misnomers because they are generally unitless ratios and therefore do not have the units of viscosity. In any case, the relative viscosity is simply the ratio of the

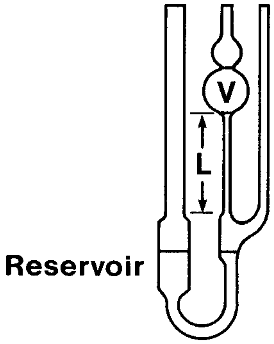


Figure 2.7 Schematic diagram of a viscometer. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

viscosity of the polymer solution to the viscosity of the pure solvent at the same temperature. Since the time t is the only quantity on the right-hand side of equation (14) that varies, the "relative viscosity" is simply the ratio of the two efflux times, and is given by

$$\eta_{rel} = \eta_{soln} / \eta_{solvent} = t_{soln} / t_{solvent} > 1.0 \tag{16}$$

The relative viscosity (a misnomer since it is a unitless ratio) is larger than unity since the dissolved polymer molecules impede the flow of solvent. The specific viscosity, defined by

$$\eta_{sp} = \eta_{rel} - 1.0 \tag{17}$$

quantifies the viscosity increase itself by subtracting unity from the relative viscosity. The higher the concentration of polymer in the solution the higher will be the viscosity, and the specific viscosity therefore has to be divided by the concentration, to give the quantity η_{sp}/c. The units of concentration chosen are typically g/dl, where a deciliter is a tenth of a liter. This is done so that the intrinsic viscosity obtained from these quantities generally has a value that is conveniently between 0.1 and 10.

The two extrapolations used to obtain the intrinsic viscosity are described by equations (18) and (19),

$$\eta_{sp}/c = [\eta] + k' [\eta]^2 c \tag{18}$$

$$\ln(\eta_{rel})/c = [\eta] - k'' [\eta]^2 c \tag{19}$$

and by Figure 2.8. The two Huggins constants k' and k'', which determine the slopes of the two extrapolation lines, are frequently reported in viscometric studies. Unfortunately, they do not yield a great deal of useful molecular information. It is known, however, that k' and k'' should add algebraically to 1/2, with k'' usually being negative and smaller in magnitude than k'.

Typical viscometric plots are shown schematically in Figure 2.8, where the two extrapolations yield the intrinsic viscosity. For many polymer-solvent systems a value of 2.0 dl g^{-1} would correspond to a molecular weight in the vicinity of a million.

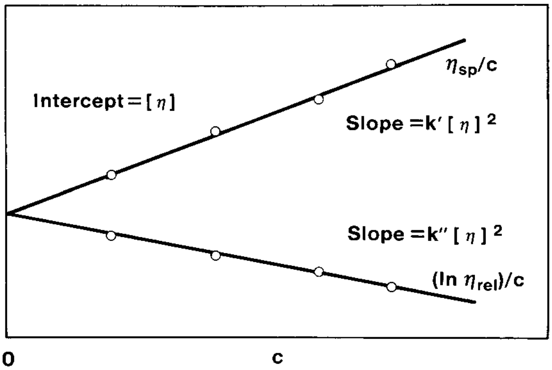


Figure 2.8 Double extrapolations of viscosity data to obtain the intrinsic viscosity $[\eta]$. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

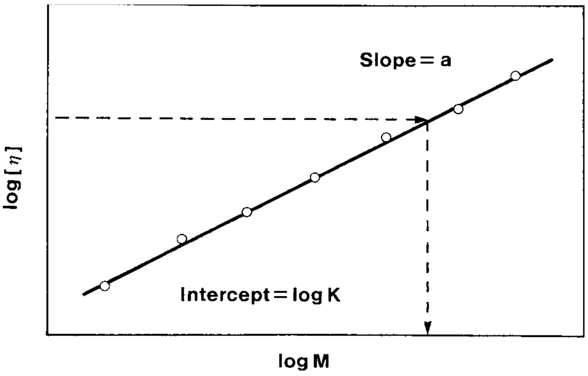


Figure 2.9 Calibration of intrinsic viscosity results. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

In order to obtain molecular weight values from intrinsic viscosities it is necessary to use the calibration illustrated in Figure 2.9. It is based on the Mark–Houwink relationship, which is given by

$$[\eta] = KM^a \tag{20}$$

where K and a are constants that depend on polymer, solvent, and temperature. Typical values are $K = O(10^{-4})$ and $a = 0.7$. A typical calibration curve is shown schematically in Figure 2.9. The intercept gives a value for the constant K, and the slope yields a value for the constant a. These constants have been tabulated for many polymer-solvent-temperature combinations.[32–34]

The main advantages of the viscometric technique are (a) the simplicity of the method, and (b) the range of molecular weights that can be measured. The main disadvantage is the fact that the method must be calibrated.

2.1.4 Uses for Molecular Weights

There are several important reasons for wanting to know molecular weights in polymer science. From the viewpoint of inorganic polymers, the main uses are for the interpretation of molecular-weight dependent properties, and for the elucidation of polymerization mechanisms. The latter involves characterization of the molecular weight distribution, which is the subject of the following section.

2.2 Molecular Weight Distributions

2.2.1 Importance

The subject of molecular weight distributions is of great practical as well as fundamental importance. For example, a small amount of material of either very low molecular weight or very high molecular weight can greatly change solid and liquid state properties, and thus affect the processing characteristics of a polymer. Therefore, it is necessary to develop quantitative ways for characterizing molecular weight distributions.

2.2.2 Representation of Molecular Weight Distributions

One way to characterize a distribution is shown in Figure 2.10, where W_M is the weight fraction of polymer that has a molecular weight in an infinitesimal interval about the specified value of M. This is the so-called differential representation of the distribution, and the two curves shown are for a relatively narrow distribution (A) and a relatively broad one (B). Such curves provide all the quantitative details of the distribution. For example, they indicate what percentage weight of the polymer has a molecular weight above or below a specified value of M, or between two specified values (as shown by the hatched segment under one of the curves). Also, the maximum in the curve locates the most probable value of M. It is also immediately obvious whether the distribution is unimodal (one maximum), or multimodal (often bimodal). Such information can help to elucidate a polymerization mechanism, particularly if it is available for polymers having different extents of polymerization (usually obtained by using different polymerization times). For example, a bimodal distribution could indicate that some of the polymer was formed at a catalyst surface and some in solution. Bimodal distributions have, in fact, been observed in both polyphosphazenes[35] and polysilanes.[36] Illustrative results for a phosphazene polymer are shown in Figure 2.11.[35]

The simplest measure of the breadth of a distribution is the ratio of two different types of average molecular weight. Specifically the ratio of M_w to M_n is by far the most widely used for this purpose, and is called the "polydispersity index." It has a minimum value of unity (for a monodisperse material in which all the chains have exactly the same length). The extent to which it exceeds unity is a measure of the breadth of the distribution. Typical values are in the range 1.5–2.0, but many polymerizations yield considerably larger values.

2.2.3 Experimental Determination

The most direct way to obtain a molecular weight distribution such as the one illustrated in Figure 2.10 is to separate the polymer into a series of fractions each of which has a

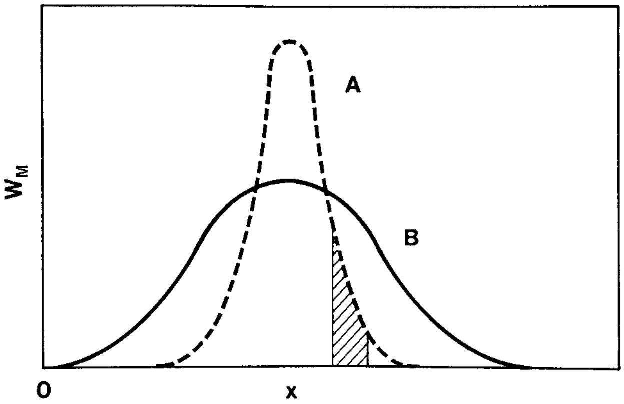


Figure 2.10 Typical differential distribution curves for the molecular weight. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

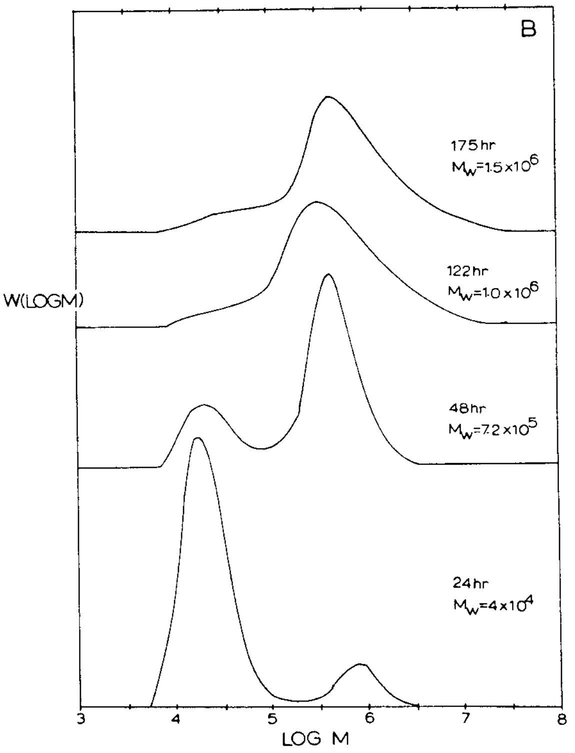


Figure 2.11 Differential distribution curves for poly[bis(trifluoro-ethoxy) phosphazene] shown as a function of extent of reaction (polymerization time).[35] Reproduced by permission of Marcel Dekker, Inc.

considerably narrower distribution. An advantage of this approach is the fact that these fractions can also be used to determine structure–property relationships that are not complicated by excessive polydispersity. This is shown by the family of curves making up the outer curve in Figure 2.12. The simplest technique for achieving such a separation is based on the decrease in polymer solubility which occurs as the molecular weight is increased, as is illustrated in Figure 2.13. Thus, lowering the temperature of a polymer solution can decrease the solubility of the polymer sufficiently to cause precipitation of the highest molecular weight material. This fraction might have a molecular weight of M_1 or higher, as is illustrated by the corresponding region in the Figure. Removal of this fraction, followed by subsequent cooling of the remaining solution, could then be used to produce a fraction in which the molecular weights are primarily in the range M_2 to M_1, and so on. It is also possible to decrease the solubility of the polymer by adding a non-solvent to the solution. This method is used more frequently than the method that uses cooling.

Another technique for separating a polymer into fractions is called Solvent Gradient Elution. In it, the unfractionated polymer is deposited as a very thin coating on high-surface-area beads in a chromatographic column. A very poor solvent for the polymer is then allowed to flow over the particulate material, thereby extracting only the lowest molecular weight (most soluble) material. A controlled amount of a good solvent for the polymer is then added to the first solvent, and then this mixture used to extract polymer of somewhat higher molecular weight. Carrying out this process n times,

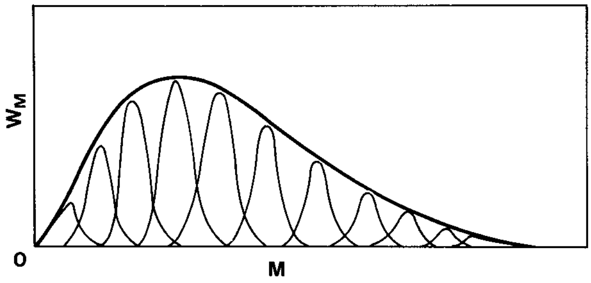


Figure 2.12 Resolution of a broad distribution curve into contributions from its constituent fractions. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

up to complete dissolution of the polymer, then yields *n* fractions of the material. The main disadvantage of this technique results from the fact that it works best only if an equilibrium can be established between dissolved and insoluble polymer. This is inherently difficult since shorter chains may be prevented from escaping into solution because they are entangled with longer molecules in the sample. On the other hand, the fractional precipitation technique is generally carried out in dilute solution, where each chain can participate in the partitioning process between solution and precipitated phase completely independently of the other chains. The main advantage of the gradient elution technique is the ease with which it can be automated.

The most modern technique for fractionating polymers is called Gel Permeation Chromatography (GPC). The packing in the chromatographic column consists of cross-linked polystyrene beads swollen with a convenient solvent, as is illustrated in Figure 2.14. The polymer to be fractionated is dissolved in the same solvent and the solution is then forced through the packing. The smaller the polymer molecule, the more likely it will be able to enter the various "caves" or interstices between the chains that make up the swollen network structure. This slows the passage of the smaller polymer chains through the packing. Thus, each subsequent fraction collected has a molecular weight smaller than its predecessor. This technique is also relatively easy to automate.

The determination of molecular weights and their distributions is almost always the first technique used to characterize polymers, and this is especially true for inorganic polymers. Additional techniques used to characterize other features of polymeric materials are described in the following sections.

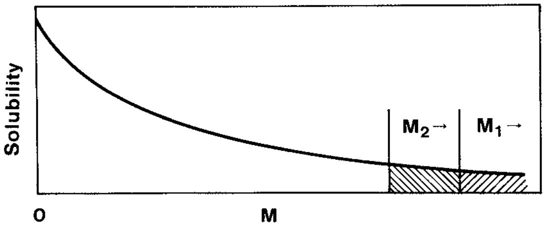


Figure 2.13 The decrease in solubility with increase in molecular weight that serves as the basis for the fractional precipitation technique. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

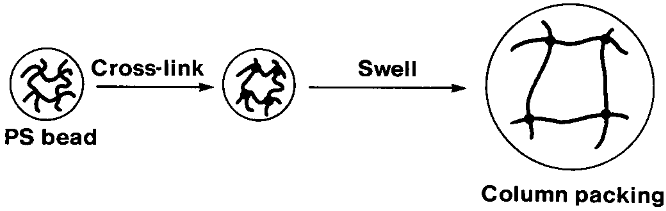


Figure 2.14 Preparation of swollen, cross-linked beads for gel permeation chromatography. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

2.3 Other Structural Features

2.3.1 Backbone Bonding

A knowledge of the molecular weight of a polymer provides information about the number of backbone or skeletal bonds per molecule.[37,38] But the skeletal bonds require additional characterization. The most important item of information that needs to be determined is the length of each bond. In this regard inorganic polymers are quite different from their organic counterparts. Specifically, virtually all covalent bonds between pairs of atoms in inorganic polymers (Si, P, N, etc.) are longer than the C-C bond found in organic polymers. Thus, inorganic polymers are much less "congested" and, as a consequence, much more flexible.[39–42] They are more flexible both in the equilibrium sense, which means that they can form more compact random coils, and in the dynamic sense, which means they can readily switch between different spatial arrangements. The first of these factors has a powerful influence on the melting point of a polymer. The second influences the temperature below which the polymer becomes a glass.[43]

The melting point of any crystalline material is given by

$$T_m = \Delta H_m / \Delta S_m \tag{21}$$

where ΔH_m is the heat of fusion and ΔS_m is the entropy of fusion. Since inorganic polymers can adopt very compact random-coil arrangements of high entropy, their entropies of fusion are frequently very high, and their melting points relatively low. Of course exceptions can occur, particularly when unusually strong intermolecular attractions give an atypically large heat of fusion.

The glass-transition temperature T_g is the temperature below which the polymer is glass-like because long-range motions of the polymer chains are no longer possible. The more flexible the polymer, in the dynamic sense, the lower is the temperature to which it can be cooled before this flexibility is "frozen out." Thus, the high dynamic flexibility generally enjoyed by inorganic chains frequently generates relatively low glass transition temperatures as well. The glass-transition temperature is of considerable practical, as well as fundamental importance. For molded objects, it closely approximates the empirically defined "brittle point" of a polymer. This has little

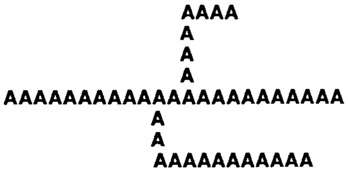


Figure 2.15 Branching in the homopolymer poly(A).

influence on the properties of films and fibers, however. After all, glass wool is far below its glass-transition temperature at room temperature, yet it is clearly not brittle. The same is true for polystyrene film, which is used extensively as a packaging material.

2.3.2 Branching and Cross-Linking

Under some conditions, branches can grow from the chain backbone, as shown in Figure 2.15. This could occur, for example, during a polymerization process, as in the case of the formation of some phosphazene polymers. It could also occur subsequently, through processes such as high-energy irradiations, and the generation of free radicals. Because branch points represent irregularities in the chain structure, they can greatly suppress the tendency of a polymer to crystallize. Branching can occur to the extent that a *network* is formed, as in the preparation of thermosetting epoxy resins, or in the curing of elastomers. This is illustrated in Figure 2.16. In some cases, such cross-linking can be highly disadvantageous, since it can make the material impossible to manipulate or fabricate.

2.3.3 Chemical and Stereochemical Variability

Homopolymers possess only one type of repeat unit in the chain structure. Thus, except for the chain ends, the composition is constant throughout the chain. It is also possible to prepare chemical *copolymers*, in which two chemically different repeat units are distributed along the chain backbone. In *terpolymers*, there are three different types of repeat units. A chemically copolymeric polyphosphazene is shown in Figure 2.17. Thus, copolymers involve a composition variable since, for example, an AB copolymer

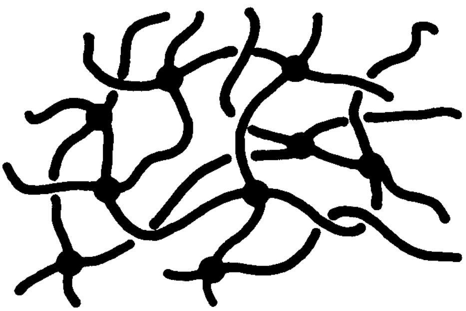


Figure 2.16 Network formation in a polymer, with the dots representing cross-links. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

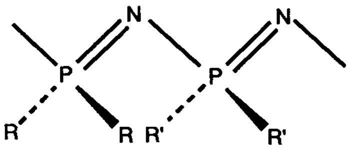


Figure 2.17 Sketch of a copolymeric polyphosphazene.

could contain from 0 to 100 mol % of repeat unit A. In this respect an analogy can be made with mixtures or solutions of small molecules. Chemical copolymers have an additional variable, that is unique to systems that consist of covalently bonded chains. This is the order, or sequencing, in which the different units are organized along the chain. For example, even at 50 : 50 equimolar composition, a copolymer could have any of the following sequential structures:

1. ABABABABABABABABABABAB Alternating
2. ABBAAABABBBBAABBBAAAAB Random
3. AAAAAAAAAAABBBBBBBBBBB Diblock
4. AAAAAABBBBBBBBBBBAAAAA Triblock

The alternating structure (1) does not generate unusual properties since it is equivalent to that of a homopolymer having AB as the repeat unit. A random copolymer structure (2) can give rise to useful properties, in spite of the fact that many of the properties of this type of copolymer are some simple average of the properties of the all-A and all-B parent homopolymers. One use for this type of structure is to introduce sufficiently irregular sequences into the polymer to prevent crystallization. This approach is used in the design and synthesis of ethylene-propylene elastomers. Other copolymer units can provide potential cross-linking sites, as do the vinyl side groups in dimethylsiloxane-methylvinylsiloxane copolymers.

The two block-like structures (3 and 4) are generally of the greatest interest. If the blocks are relatively long, typically 20 or more repeat units, the two types of sequences will be incompatible and the system will undergo microscopic phase separation. Domains that contain repeat units of one type only, and having dimensions the order of 200 Å, will be formed within a continuous phase of the other type. Such multi-phase materials can have very important mechanical properties. For example, in the triblock copolymer, chains that have crystalline or glassy end blocks and elastomeric center blocks can form thermoplastic elastomers. The crystalline or glassy domains at the ends of the elastomeric sequences serve the same role as the cross-links in a conventially cross-linked material. However, these elastomers are reprocessible in the sense that heating them above the melting point or glass-transition temperature of the end blocks temporarily breaks up the network structure. Two important examples are the styrene-butadiene-styrene copolymers (the Kratons®),[38] illustrated in Figure 2.18, and diphenylsiloxane-dimethylsiloxane-diphenylsiloxane copolymers.[44]

If the chain backbone contains atoms that are unsymmetrically substituted, then stereochemical variability becomes possible. Stereochemical copolymers have repeat units that are chemically identical but stereochemically different, and in a sense these parallel the chemical copolymers already described. If substituted skeletal atoms in adjacent repeat units have the same atomic configuration, then the placement is said to

Figure 2.18 Example of a reprocessable elastomer, with the cross-linking polystyrene domains shown by the circles. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

be *meso*; placements with opposite configurations are called *racemic*. Polymers having long *meso* sequences are called isotactic and those with long *racemic* sequences, syndiotactic. Because of their stereoregular structure, these polymers can generally crystallize. If *meso* and *racemic* placements occur at random along the chain, the polymer is described as being atactic, and is generally incapable of crystallization. Some examples of stereochemically variable chains are shown schematically in Figure 2.19. The importance of crystallinity in polymers is discussed in several subsequent sections, and specific cases involving polysiloxanes are described in Chapter 4.

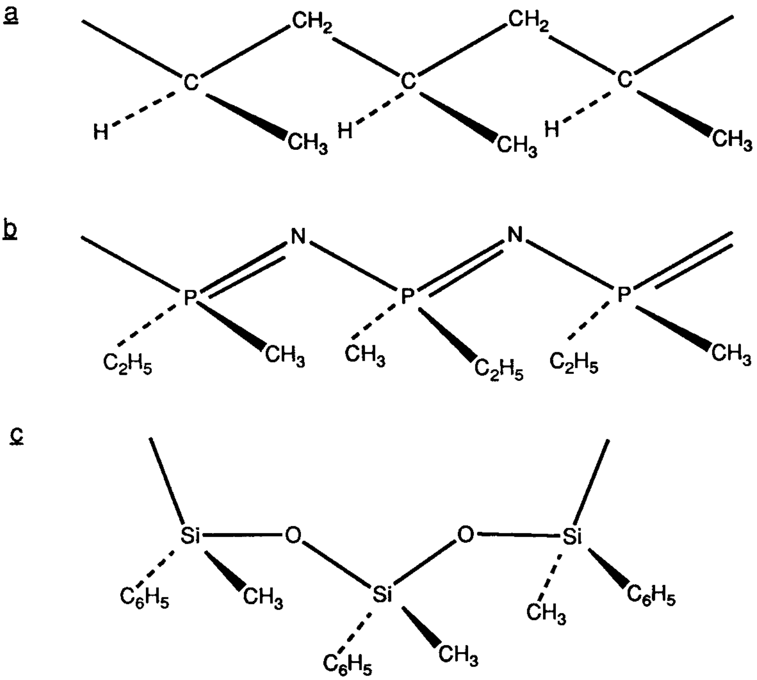


Figure 2.19 Sketches of some stereochemically variable chains, of polypropylene (two *meso* placements), poly(methyethylphosphazene) (two *racemic* placements), and poly(methylphenylsiloxane) (*meso* placement followed by *racemic* placement).

2.4 Chain Statistics

2.4.1 Basic Goals

In this research area, the goal is to characterize the spatial arrangements or configurations of a chain molecule. This is most commonly accomplished in terms of the overall *size* of the molecule, typically in a random-coil state.[7,39,40,42] More specifically, the quantities of interest are the mean-square end-to-end distance or dimension $<r^2>$ of the chain as illustrated in Figure 2.20, or its mean-square radius of gyration. These measures of the size of the polymer domain can be obtained directly from light scattering or neutron scattering[45] or, somewhat indirectly, from solution viscosities. The experimental results are then compared with theoretical predictions obtained by the use of realistic models of the chain molecule.

2.4.2 Illustrative Models

The simplest model of this type is called the freely jointed chain, and is illustrated in Figure 2.21. In it, the skeletal bonds are joined end to end, but are completely unrestricted in direction. This is clearly a situation not found in a real polymer (bond angles in real polymers are relatively fixed). It is also assumed that the chains have zero cross-sectional area, that is that the chains are unperturbed by excluded-volume effects. These effects arise because atoms of a chain exclude from the space they take up all other atoms from all other chains. They are related to excluded-volume effects occurring even in systems as simple as real gases. The expression for the mean-square end-to-end distance of such an idealized chain is particularly simple:

$$<r^2>_0 = nl^2 \tag{22}$$

where $<r^2>_0$ is called the unperturbed dimensions, and n is the number of skeletal bonds, of length l. Values of $<r^2>_0$ calculated for more realistic models, or obtained for real chains by experimental measurements, are then compared to nl^2, in what is called the "characteristic ratio," $<r^2>_0/nl^2$. The extent to which this ratio exceeds unity is a measure of the extent to which the unperturbed dimensions of a revised chain model, or of a real polymer chain, differ from those of the freely jointed model. In the limit of a very large value of n, it is frequently given the symbol C_∞.

Figure 2.20 Representation of the end-to-end distance of a random-coil polymer. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

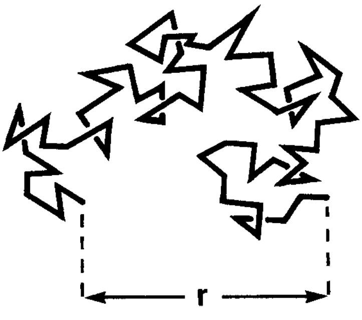


Figure 2.21 Sketch of a freely jointed chain. The bonds, represented by the straight lines, are uncorrelated in direction. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

The first of the more sophisticated models takes into account the fact that bond angles in molecules are very nearly constant. It also assumes that rotations about the skeletal bonds are unhindered (low-energy barrier). This model has become known as the freely rotating chain. For tetrahedral bonding, this modification approximately doubles the characteristic ratio, to 2.2. The ratio is generally increased further if it is assumed that different rotational angles have different energies. The final refinement involves taking into account the cooperativity of neighboring rotational isomeric states: in other words it assumes that the conformation of one skeletal bond influences the conformation of the neighboring skeletal bonds. The extent to which the final two modifications affect the characteristic ratio depends on the detailed geometry of the chain and its conformational preferences. Most *experimental* values of the characteristic ratio are in the range 4–10. Melting points generally increase with increase in the value of the ratio, since it is an approximate measure of the equilibrium stiffness of a polymer chain.

2.4.3 Other Configuration-Dependent Properties

Although the unperturbed dimensions have been used mainly to characterize spatial configurations, other properties are also being used for this purpose. Among these are:

- Mean-square dipole moments
- Strain birefringence and dichroism
- Optical rotation
- Nuclear magnetic resonance (NMR) chemical shifts
- Cyclization equilibrium constants
- Stereochemical equilibrium constants

In a typical analysis of a polymer chain, the *experimental* values of configuration-dependent properties and their temperature coefficients are compared with the results of rotational isomeric state *calculations*. These comparisons yield values of the energies for the various rotational states about the backbone bonds, and these conformational preferences can then be used to predict other configuration-dependent properties of the chains. It is also possible to obtain such conformational information from potential energy calculations, using the methods of molecular mechanics.[39,46–52]

2.4.4 Minimum Energy Conformations

Completing the conformational analysis of a polymer chain in either way can yield an important bonus. Such an analysis immediately identifies the conformation having the lowest intramolecular energy. This is important, because the lowest energy conformation is almost always the one adopted by the chain when it crystallizes. Thus, the conformation assumed by a polymer chain depends almost entirely on intramolecular interactions, even though crystallization is a highly cooperative process, in which *inter*molecular interactions must occur in profusion. Apparently, only after a regular conformation is chosen by a single chain does the question arise about how it is going to pack with its neighbors in a crystalline lattice.

Very early examples in this area are the predictions that polyethylene should crystallize in a planar zig-zag conformation, poly(oxymethylene) in a helix having nine repeat units per five turns, some isotactic poly(α-olefins) in helices having three repeat units per single turn, and a number of polypeptides and proteins in the now-famous α-helices. All these predictions, and many others, have been confirmed experimentally.[39]

Another example that is much more recent and more relevant to inorganic materials, pertains to conformational energy calculations carried out on the polysilane sequence sketched in Figure 2.22.[53,54] The results, as is customary, are presented as a map, as shown in Figure 2.23.[54] In this representation, contours of equal energy are plotted as a function of the two rotational angles about adjacent skeletal bonds in the central portion of the chain sequence. As shown in the Figure, the minimum energy conformations should occur at rotational angles of approximately ±120°, to generate a helix very similar to that formed by poly(oxymethylene). Thus, it is predicted to be very different from the all-*trans*, planar zig-zag conformation preferred by its hydrocarbon analogue, polyethylene.

2.5 Solubility Considerations

2.5.1 Basic Thermodynamics

It is generally more difficult to find a solvent that will dissolve a polymer than it is to find a solvent for a small molecule such as, for example, the monomer from which the

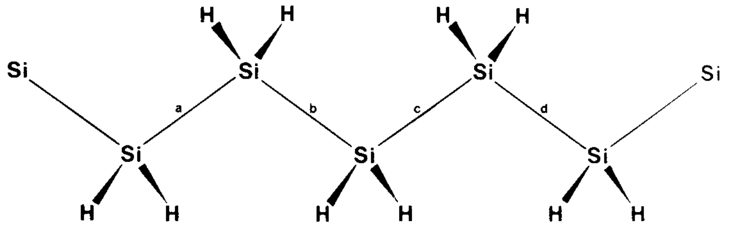


Figure 2.22 Sketch of a bond sequence in polysilane itself.[54] Reprinted by permission of the American Chemical Society.

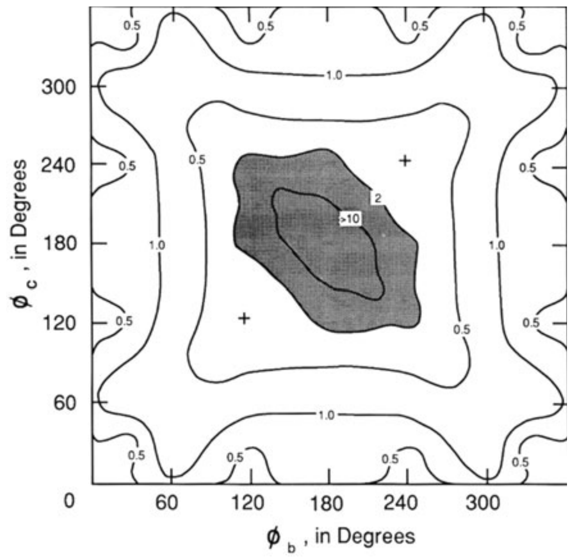


Figure 2.23 Conformational energy map for the polysilane sequence shown in Figure 2.22, where ϕ_b and ϕ_c are the rotational angles about skeletal bonds b and c in this figure. The contour line labelled 2 encloses regions corresponding to very high energy, greater than 2 kcal mol^{-1}. The two plus signs locate the conformations of minimum energy.[54] Reproduced by permission of the American Chemical Society.

polymer was prepared. This is understandable by a consideration of the free-energy change for the dissolution process:

$$\Delta G_{\text{dis}} = \Delta H_{\text{dis}} - T\Delta S_{\text{dis}} \tag{23}$$

where ΔH_{dis} and ΔS_{dis} are the enthalpy and entropy of dissolution, respectively. Usually, the interactions between unlike species are unfavorable, and the enthalpy change is positive (the energy increases). Since the free energy change must be negative for the process to occur (at constant temperature and pressure), the second term must be negative and predominate over the first. That is, dissolution processes are generally entropically driven.

2.5.2 Problems Specific to Polymers

The above conclusion is unfortunate for the case of polymeric solutes, because their entropies of dissolution are unusually small. The repeat units can not become as disordered as can the corresponding monomer molecules since they are constrained to be part of a chain-like structure. Such disordering is particularly difficult if the chain is stiff. Thus, in this situation dissolution is even less likely. Crystalline polymers are also more difficult to dissolve than are their amorphous counterparts since the enthalpy of dissolution also contains a large, positive contribution from the latent heat of fusion.

The above equation also explains why two different *polymers* are seldom miscible. Both solute and solvent are now polymeric and thus both suffer from the entropy decreases described above. It also explains why it is necessary to heat a mixture in which the solute does not dissolve at room temperature. This increase in T increases the magnitude of the last term in equation (23), and this is the term that generally makes the free energy change negative.

2.5.3 Solubility Parameters

Definitions

As already mentioned, interactions between unlike species are generally unfavorable. This observation is, in fact, the basis for the rule of thumb that "like dissolves like." This rule is obviously very qualitative, but it has now been sucessfully extended to provide a quantitative basis for finding potential solvents for a polymer. In the theory of Hildebrand, it is acknowledged that ΔH_{dis} is almost certainly going to be positive. The goal is then to find a means to make ΔH_{dis} as small as possible. Specifically, it is given by the equation

$$\Delta H_{dis} = v_1 v_2 (\delta_1 - \delta_2)^2 \quad (24)$$

where it is written as the product of the volume fraction of solvent, the volume fraction of polymer, and the square of the difference between the values of a molecular characteristic called the "solubility parameter,"[55] δ for the solvent and polymer, respectively. The quantity δ is defined by

$$\delta = (\Delta E/V)^{1/2} \quad (25)$$

that is, as the square root of the cohesive energy density, which is the ratio of the molar energy of vaporization to the molar volume of the liquid. Thus, the quantity δ is a measure of the strength of the interactions between the molecules of a substance, since vaporization involves greatly increasing the average distance of separation between them. Two molecules are "like" one another if the strengths of their interactions are similar. The two values of the solubility parameter will then be similar, and this will minimize the positive value of ΔH_{dis}, as shown in equation (24). The utility of the approach is based on the fact that values of δ have been determined for many solvents and polymers by both experiment and approximate calculations. Solubility is likely to occur when a polymer and solvent have solubility parameters within one and a half units of each other, when the units are in calories and cm^3.

Experimental Determination, Solvents

It is relatively easy to determine the solubility parameter of a solvent. The molar volume can be obtained from pycnometry, or a value can possibly be found in the literature. Also, since most solvents of interest have significant volatility, their heats of vaporization can be determined calorimetrically. The experimentally determined heat of vaporization can be converted into the desired energy of vaporization through a conversion term that is simply the change in pressure-volume product for the process. Specifically, $\Delta H = \Delta E + \Delta(pV)$. At constant pressure this is $p\Delta V$ and, to the adequate approximation that the vapor is an ideal gas, the conversion term is thus simply RT (where R is the usual gas constant).

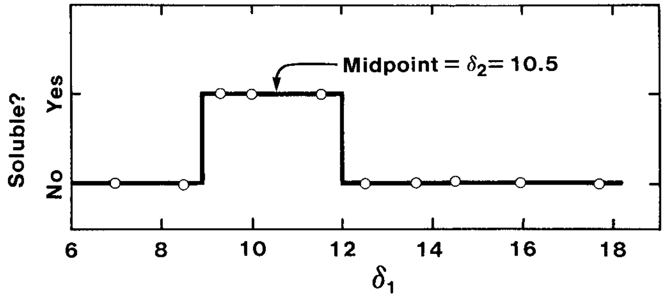


Figure 2.24 Solubility bar graph for determining the solubility parameter δ_2 for a polymer. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

Experimental Determination, Polymers

Polymers degrade before they vaporize, so indirect methods must be used to determine their solubility parameters. The simplest of these methods is a two-valued bar graph, as is illustrated in Figure 2.24. A series of solvents of known solubility parameter δ_1 are used. Each is tested to determine if it is a solvent for the polymer. The "yes" or "no" answers are then plotted at different heights along the δ_1 abscissa. The value of δ_1 corresponding to the midpoint of the "yes" bar is taken to be the solubility parameter δ_2 of the polymer. This is a reverse application of equation (24). The argument is now that solvents that are found to dissolve the polymer must have solubility parameters close to the unknown solubility parameter of the polymer.

An alternative approach is to measure the minimum temperature required to bring about dissolution of the polymer, again in a series of solvents of known solubility parameters. This is illustrated in Figure 2.25. The solubility parameter of the polymer is taken to be the value of δ_1 that corresponds to the smallest required increase in temperature.

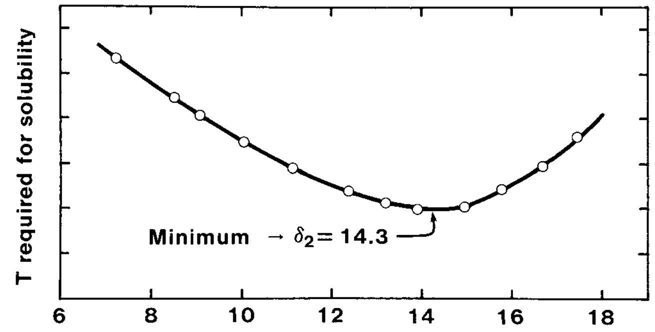


Figure 2.25 The dissolution temperature method for determining polymer solubility parameters. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

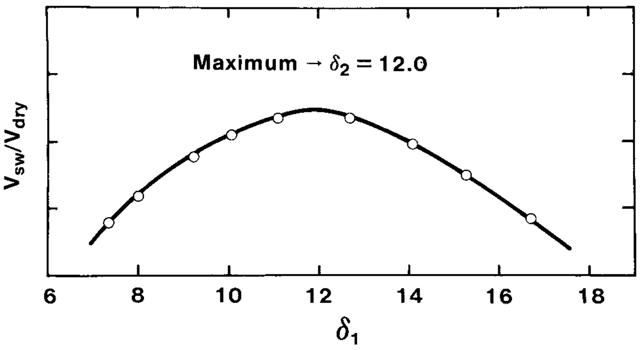


Figure 2.26 The network swelling method for determining polymer solubility parameters. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

If a cross-linked sample of the polymer of interest is available, then it is possible to determine δ_2 from swelling equilibrium measurements. Portions of the sample are weighed and are then placed into each of a series of solvents of known solubility parameters. The polymers are allowed to swell by imbibing the solvent. After the swelling is complete, each sample is reweighed, and the weights and specific volumes of polymer and solvent are used to calculate values of the ratio of the swollen to dry volume of the sample. These values are then plotted against the solubility parameters of the solvents, as shown in Figure 2.26. The largest value of the ratio, or the highest degree of swelling, must be that obtained by using the best solvent for that polymer. Therefore, the solubility parameter of the polymer must be at least approximately equal to δ_1 for this particular solvent. A similar approach would be to search for the maximum intrinsic viscosity when the *uncross-linked polymer* is dissolved in the same series of solvents.

If short chains, or oligomers, of the polymer of interest are available, it is possible to use extrapolation techniques to obtain δ_2. The oligomers are chosen to have low enough molecular weights that the required energies of vaporization can be determined experimentally. The resultant values of δ_2 are then plotted against the reciprocal of the molecular weight and the curve is extrapolated to infinite molecular weight, as shown in Figure 2.27. The intercept corresponds to the solubility parameter for the high-molecular-weight polymer.

A final method for obtaining solubility parameters, for solvents as well as for polymers, involves a theoretical approach called a group additivity scheme.[49,56,57] First it is necessary to determine how much each atom or chemical group contributes to the solubility product of a molecule. (For example, the contribution from a methylene group is simply the change in solubility parameter observed in changing from ethane to *n*-propane.) Such contributions have been tabulated extensively in the literature. The appropriate group contributions are then added together to predict the solubility parameter of the entire solvent molecule. In the case of a polymer, the contributions from the groups in the *repeat unit* are added. Since the solubility parameter is a ratio of molar quantities, the value for the repeat unit is equal to that of the polymer.

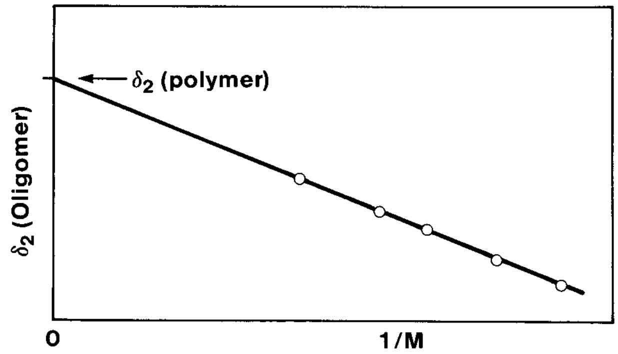


Figure 2.27 Extrapolating solubility parameters for oligomers to obtain polymer solubility parameters. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

Finally, companies such as Accelrys (San Diego) are now marketing software for calculating solubility parameters directly, by separately simulating energies of vaporization and specific volumes.[58–60]

Trends

Actual values of solubility parameters show the same trends for both solvents and polymers. Non-polar molecules and repeat units have weak intermolecular forces, small energies of vaporization, and therefore small solubility parameters. As might be expected, increased polarity increases the solubility parameter, and hydrogen bonding gives the largest values of all.

Applications

The fundamental idea is to determine the solubility parameter of the polymer, and then to use tabulated results to identify a number of solvents that have solubility parameters close to this value. The list of potential solvents is then narrowed to two or three candidates. Solvents that are too volatile, too toxic, too flammable, too expensive, and so on can be removed from the list. Other criteria would depend on the nature of the studies to be pursued. If the objective is to carry out light-scattering measurements, the need for maximizing the contrast factor would make the index of refraction of the solvent an additional important consideration.

Another application would be to minimize the swelling of a cross-linked elastomer in contact with a solvent. In this case, of course, one would be looking for a polymer giving the largest *mismatch* with the solubility parameters of the solvent to which the elastomer was to be exposed.

It is important to note that these predictions are for the possible miscibility or immiscibility of two *amorphous* materials. They do not apply to crystalline polymers because of the neglect of the already-mentioned positive heat of fusion. However, the

predictions would be useful, for temperatures above which the polymer would no longer be crystalline.

It should also be mentioned that polymer–solvent interactions can be characterized by the second virial coefficients that appear in equations (8) and (13) and by the free energy of interaction parameter χ_1 that appears in the Flory–Huggins theory of polymer solution thermodynamics.[1,61]

2.5.4 Useful Modifications of Structure

A final comment concerns two chemical modifications which could be used to increase the solubility (and processability) of rigid polymer chains.[62,63] The first involves inserting some relatively flexible "swivel joints" into the chains. This increases chain flexibility, configurational entropy, and the entropy of mixing. The entropy of mixing can also be increased, for constant backbone rigidity, by employing very flexible side chains to mix with the solvent. Both changes decrease the free energy of dissolution, and thus increase the chances for miscibility.

2.6 Crystallinity

2.6.1 Importance

As mentioned earlier, crystallinity in a polymer is important in many applications. It is a way by which the chemist introduces solidity or hardness, but it can also have a beneficial effect on a variety of other mechanical properties.[64–67] The most important of these is probably the impact resistance of the material. Because polymer chains are so long, different segments of the same chain become incorporated into different micro crystallites. Figure 2.28 illustrates the situation. As a result, much of the polymer that connects crystallites is badly entangled and poorly positioned for crystallization. This is the reason why "crystalline" polymers typically contain 20–50% of amorphous material, and are therefore better termed "partially crystalline." The crystallites are of great importance because they give the polymer the solidity or rigidity required in many applications, for example when they are used in molded objects. The amorphous regions are also important. The chains in these regions have enough mobility that they can absorb impact energy through their skeletal motions, using frictional effects to

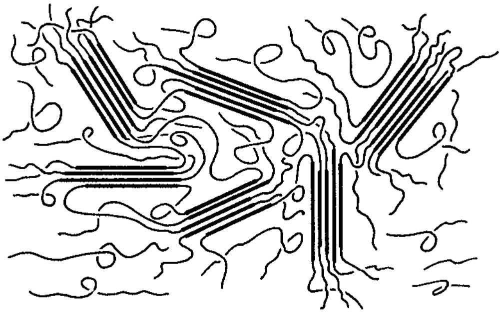


Figure 2.28 Sketch of the simplest model of a partially crystalline polymer, where the parallel straight lines represent the crystallites. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

convert the energy harmlessly into heat. A partially crystalline polymer is therefore much tougher than the same polymer would be if it were 100% crystalline.

2.6.2 Requirements

Because crystallinity is frequently highly desirable, it is important to establish the structural features that are conducive to achieving it. Most important, considerable regularity in chain structure is generally required. Specifically, crystallization is usually impossible for chain sequences that contain defects such as branch points, cross-links, chemical irregularities (comonomeric units), stereochemical irregularities (atactic placements), head-to-head placements (instead of head-to-tail placements), and so on. An interesting exception occurs when two different side groups are similar in size, and can replace one another in the crystalline lattice. In this case, even chains that are irregular in this sense can undergo crystallization.

Strong intermolecular attractions are also conducive to crystallization. They increase the heat of fusion, since fusion generally involves increasing the distance of separation between chains. The stronger the attractions, the higher the heat of fusion. Because the melting point is directly proportional to the heat of fusion, as shown in equation (21), it too is increased. The higher the melting point, the greater the degree of super-cooling that is likely to exist at any given temperature of application, and thus the greater the likelihood of crystallization.

2.6.3 Characterization of Crystallinity

Intramolecular

X-ray diffraction analysis can be used to characterize the crystallites themselves.[15,68] First, it is possible to obtain information about the chain conformation adopted by the polymer chains in the crystallites. Many polymers crystallize in helical conformations. These can be defined by the following helical parameters. The designation ρ_n tells how to rotate and simultaneously translate along an axis to generate the specified helix. First a point of reference is rotated around the proposed axis by n/ρ times a complete rotation of 2π. Simultaneously, there should be a translation of n/ρ of the crystallographic repeat distance, a quantity that is also obtained from diffraction data. Repetition of this scheme gives a helix having ρ repeat units in n turns of the helix.

Helices, like threads on screws, have a handedness or chirality. The handedness can be determined by curving the fingers of the right hand so as to follow the chain in its rotation around the axis of a drawing or model of the proposed helix. If the thumb points in the direction of the translation, then the helix is right handed, as is illustrated in Figure 2.29. If, instead, the left hand has to be used to achieve this relationship between rotation and translation, then the helix is left handed.

Intermolecular

The chains, now characterized in terms of intramolecular features, can also be characterized with regard to how they pack themselves into ordered arrangements in crystallites. This is understood in terms of the "unit cell," which is the simplest volume by means of which the entire crystallite can be generated by translations in three directions.

Figure 2.29 A right-handed helix. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

To characterize the unit cell requires a specification of the values of the lengths *a*, *b*, and *c* of the three sides, and the angles between them, if they are different from 90°. This is illustrated in Figure 2.30. Sliding the unit cell in the directions *a*, *b*, and *c* would then generate the macroscopic crystallite.

If the numbers and types of atoms present in the unit cell are also known, then it is possible to calculate the limiting or maximum density, that is, the density the material would have if it were 100% crystalline. In brief, the volume of the unit cell can be calculated from the geometric information mentioned above, and the weight of its contents can be obtained by summing the atomic weights of the atoms. The maximum density is then simply the ratio of this weight to the unit cell volume. This value of the density can be used to estimate the percentage crystallinity of an actual sample of the same polymer.

The simplest polymer morphology is obtained when polymer chains crystallize from dilute solution, circumstances under which they are not badly entangled. Crystallizations of this type have been carried out for a variety of organic polymers, most notably for polyethylene. The single crystals thus formed have a lamellar or "plate-like" structure. These platelets are typically 100 Å thick and approximately 100,000 Å in the other two directions. Interestingly, the chains are found to be perpendicular to the plane of the platelet. Since the chains are much longer than the 100 Å thickness, they must be folded back and forth a large number of times. The regularity with which they do this has been a matter of controversy for some time. Crystallizable inorganic polymers should also form such single crystals, but not much has been done to study this phenomenon.

The morphology obtained by crystallizing an *undiluted* polymer can be considerably more complicated. The simplest model proposed consists of a system in which small crystallites exist, with amorphous chains attached to them like fringes on a colloidal aggregate. Such a system is called a micelle. This model is probably too simple except for a few polymers which form relatively few, very small crystallites.

It is much more common for melt-crystallized polymers to show a *spherulitic* type of structure. In this morphology, the crystallites are packed into spheres, except where

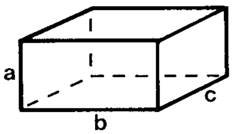


Figure 2.30 Sketch of a unit cell having a volume *abc* which, together with the weights of the atoms it contains, gives the crystallographic (maximum) density of the polymer. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

a sphere encounters another sphere or an interface. The chains also exist in lamellae, but are folded perpendicular to the radii of the spherulites. The amorphous material is located *between* the radii as they diverge in progressing from the center of the spherulite to its surface.

2.6.4 Methods for Determining Percent Crystallinity

The four methods commonly used to determine the percent crystallinity of a partially crystalline polymer are dilatometry, X-ray crystallography, infrared spectroscopy, and calorimetry.

Dilatometry

In dilatometry, specific volumes V or densities of materials are measured by use of a pycnometer, dilatometer, or density-gradient column. The data obtained are then interpreted through the equation

$$\%\ \text{cryst} = \frac{100\left[V(\text{amorph}) - V(\text{partially cryst})\right]}{V(\text{amorph}) - V(\text{cryst})} \tag{26}$$

which utilizes the specific volumes of the totally amorphous polymer, the totally crystalline polymer, and the partially crystalline polymer being characterized. The specific volume of the totally amorphous polymer is easily measured if the polymer can be quenched (cooled rapidly from a moderate temperature), or can be prepared in a non-crystallizable (atactic) form. Otherwise, it is necessary to measure specific volumes at temperatures above the melting temperature T_m and then extrapolate these data to the lower temperature of interest. The specific volume of the totally crystalline polymer, as already mentioned, can be obtained from the unit-cell data on the polymer.

The interpretation of equation (26) is very simple. The denominator represents the maximum difference that can be observed for the polymer, namely the difference between the values for the 100% amorphous polymer and the 100% crystalline polymer. The numerator is the difference observed between the 100% amorphous polymer and the actual, partially crystalline polymer. The ratio of this observed difference to the maximum possible difference is therefore the fraction crystallinity and, when multiplied by 100, is the percentage crystallinity.

Crystallography

In the crystallographic method, the X-ray scattering intensity is plotted against diffraction angle. It is then necessary to separate the observed intensity peaks into amorphous and crystalline contributions. This can be done by either raising the temperature (to melt the crystallites in the normal manner) or by adding a diluent (which can melt the crystallites by depressing the melting point). The peaks that disappear must have been due to the crystalline regions and the ones that are relatively unaffected must have been

due to the amorphous regions. The intensities I, thus identified, are then summed and used in the equation

$$\% \text{ cryst} = \frac{100\sum I(\text{cryst})}{\sum I(\text{cryst}) + \sum I(\text{amorph})} \tag{27}$$

the interpretation of which is straightforward.

Spectroscopy

The infrared spectroscopic method is the same as the X-ray diffraction method, except that the infrared band absorptions are used instead of diffraction intensities. As in the X-ray analysis method, the dependence of the spectrum on temperature or on the presence of diluent can be used to determine which bands are due to the crystalline regions, and which to the amorphous.

Calorimetry

In the calorimetric approach, it is necessary to know the heat of fusion of the totally crystalline polymer. This can be obtained from melting-point depression measurements, as described in the following section. The basic idea depends on the fact that the melting temperature is independent of the size of the system, since it is an "intensive" property. The extent to which it is depressed by the presence of solvent can be used to calculate a heat of fusion characteristic of the crystallites, irrespective of how many are present. This is therefore the heat of fusion of the 100% crystalline polymer. The fractional crystallinity in an actual sample is then the ratio of its calorimetrically measured heat of fusion per gram to that of the 100% crystalline polymer. For example, if the actual polymer has a heat of fusion of 7 cal per gram, and the 100% crystalline polymer a heat of fusion of 10 cal per gram, then the fractional crystallinity is 0.7, and the percentage crystallinity is 70%.

2.6.5 Some Additional Information from X-Ray Diffraction

Crystallite Size

The size of crystallites in a direction perpendicular to any chosen set of lattice planes can also be estimated from plots of X-ray scattering intensity against diffraction angle. Since infinitely sharp diffraction peaks occur only for crystallites of essentially infinite size, the width of a diffraction peak is an inverse measure of crystallite size. More specifically, the crystallite size perpendicular to the lattice planes giving rise to the diffraction can be obtained from the "half-width" of the corresponding peak (the range of scattering angle at half its maximum intensity).

Diffraction Patterns, Unoriented Polymers

The diffraction pattern obtained from an unoriented, partially crystalline polymer, or from a powdered crystalline material where the crystallites are unoriented, consists of a series of concentric circles. Such a pattern is illustrated in Figure 2.31.[4] Its exact pattern can be used to identify an unknown polymer. The origin of these circles can be

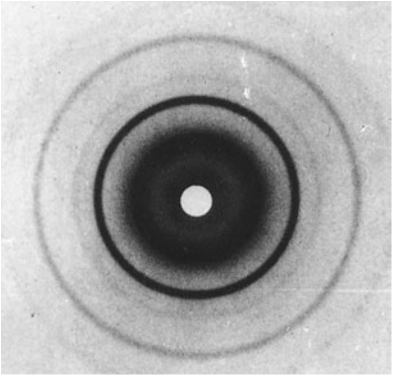


Figure 2.31 Illustrative diffraction pattern obtained from an unoriented polymer.[4] Reproduced by permission of John Wiley and Sons.

described using the Bragg diffraction law.[69] A diffraction spot will be placed on the film only where there is constructive interference, and this will occur only for those diffraction angles that obey the Bragg relationship $n\lambda = 2d \sin \theta$. Since the crystallites are completely unoriented about the incident beam, a cone of radiation is scattered for each of these permitted angles. The cone is intersected by the plane of the film perpendicular to its axis. Each intersection of a scattering cone by the film generates one of the concentric circles of the scattering pattern.

Diffraction Patterns, Oriented Polymers

The diffraction pattern obtained when the crystallites are oriented, as in a fiber, is a distinctive, symmetric pattern of arcs or layer lines. Such a pattern, obtained from a polyphosphazene, is shown in Figure 2.32.[70,71] The crystallites in the fiber have their axes nearly parallel to the fiber axis, but it is not possible to orient the other axes of the crystallites. Therefore, rotational disorder exists about the chain axes and, thus, also about the fiber axis. Because of this disorder, a vertically mounted fiber will give cones of scattered radiation above and below the incident beam. Cutting such a pair of cones parallel to their common axis gives the observed, symmetrical pair of arcs in the scattering pattern. It is the separation between a pair of arcs that gives the crystallographic repeat distance mentioned earlier. Models such as that shown in Figure 2.33[70,72] are then postulated as possible structures for the polymer.

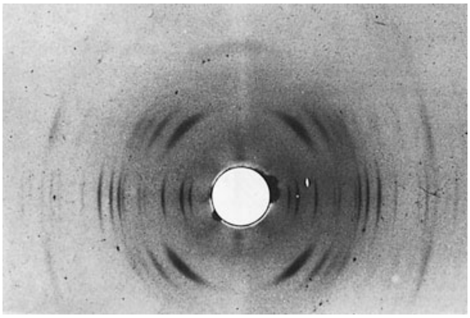


Figure 2.32 X-ray fiber diffraction pattern of poly(dichlorophosphazene). The layer-line separation distance corresponds to a polymer fiber axis repeating distance of 4.92 Å. Reproduced by permission of Academic Press.

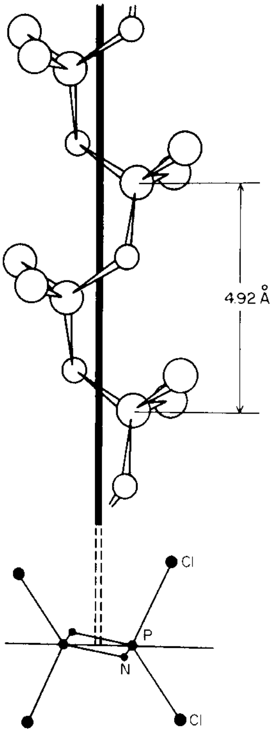


Figure 2.33 Distorted *cis-trans* planar conformation of poly(dichlorophosphazene).[70,72] Reproduced by permission of John Wiley and Sons.

2.7 Transitions

2.7.1 Definitions

The simplest definition of a *first-order transition* is one in which heat flows into or out of the material with no change in temperature. Examples are melting and boiling and their reversals, crystallization and condensation.

However, it is useful, to provide a thermodynamic definition of a first-order transition. Specifically, it is one in which there is a discontinuity in a first derivative of the Gibbs free energy. The advantage of this definition is the guidance it provides for the experimental study of phase transitions. A useful expression for the free energy in this regard is

$$dG = Vdp - SdT \tag{28}$$

where the symbols have their usual significance. (G is the Gibbs free energy, V the volume, p the pressure, S the entropy, and T the absolute temperature.) It is called one of the fundamental equations of thermodynamics since it combines the first and second laws.

The constant-temperature first derivative with respect to pressure obtained from equation (28) is

$$(\partial G/\partial p)_T = V \tag{29}$$

and is, thus, equal to the volume of the system. Therefore, studies of volume changes, called dilatometry, should be useful for characterizing first-order transitions. The constant-pressure first derivative with respect to temperature is given by

$$(\partial G/\partial T)_p = -S \tag{30}$$

and is equal to negative entropy. Thus, calorimetric measurements should also be useful.

Second-order transitions are treated similarly. Properties that are second derivatives of the free energy show a discontinuity with changes in temperature. For example, the second derivative with respect to temperature and pressure is

$$\left[\partial(\partial G/\partial p)_T/\partial T\right]_p = (\partial V/\partial T)_p = V_{av}\alpha \tag{31}$$

Here, α is the thermal expansion coefficient, $\alpha = (1/V_{av})(\partial V/\partial T)_p$, and it is this coefficient, rather than the volume itself, that will show a discontinuity in a dilatometric study. The similarly obtained equation

$$\left[\partial(\partial G/\partial T)_p/\partial T\right]_p = -(\partial S/\partial T)_p = -(\mathrm{d}q_{\mathrm{rev}}/T\mathrm{d}T)_p = -C_p/T \tag{32}$$

shows that the analogous calorimetric quantity is the heat capacity C_p.

In second-order transitions, there is no latent heat, nor discontinuous changes in volume or entropy.

2.7.2 Illustrative Representations

These conclusions are summarized graphically in Figure 2.34. The first-order transition of importance in polymer chemistry is the *melting point* T_{m}, and the top two sketches show the discontinuities ΔV_{m} and ΔS_{m} in the volume and entropy, respectively.

The *glass-transition temperature* T_{g} is thought by some to be a second-order transition, so some data relevant to it are shown in the middle two sketches. The volume and entropy merely show a change in slope at T_{g}. The second derivatives are shown in the bottom pair of sketches, with the expected discontinuities in the thermal expansion coefficient and heat capacity.

2.7.3 Dilatometric Results

Some typical, combined dilatometric results for a polymer are shown schematically in Figure 2.35. Since the volume is plotted against the temperature, there is a change in slope at T_{g}, where the polymer changes from a glass to a rubbery material, and nearly a discontinuity at T_{m}, where the crystalline regions melt to the liquid state. The melting point is generally not sharp, as shown, because the presence of crystallites that are small or imperfectly formed means that melting will occur over a range in temperatures.

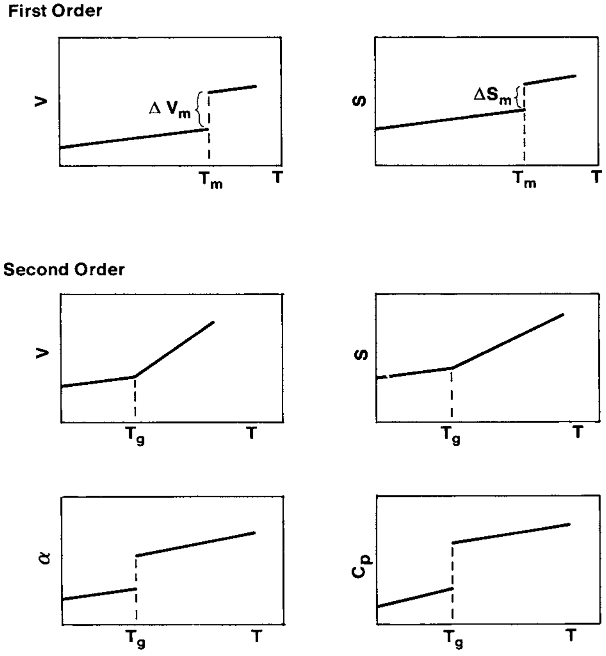


Figure 2.34 Some characteristics of first-order and second-order transitions. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

2.7.4 Calorimetric Results

Bomb Calorimetry

Analogous calorimetric results obtained in a bomb calorimeter are shown in Figure 2.36. It is a very laborious process to obtain actual values of the specific heat as a function of temperature. At each temperature a known amount of heat must be added to the polymer sample, in a sealed bomb calorimeter, and the temperature increase must be measured carefully. Because this is so time consuming, simpler techniques have been developed, and some are described in the following sections.

The polymer characterized in this figure was "quenched" so that it was completely amorphous and glassy at the low-temperature start of the experiment. As the temperature is raised, the specific heat increases because of the more pronounced vibrations of the atoms in the polymer chains. (In atomic and molecular terms, the specific heat is a measure of the number of modes a system has for taking up energy, and the efficiency with which this energy can be absorbed.)

At the glass-transition temperature, the specific heat increases abruptly because the previously frozen large-scale molecular motions are now available to the chains for the uptake of thermal energy. The subsequent sharp downturn is due to crystallization

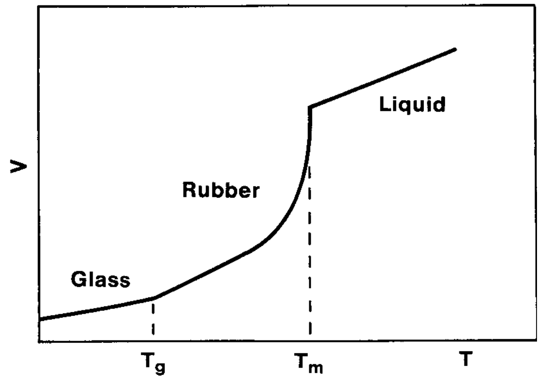


Figure 2.35 Typical dilatometric results for a partially crystalline polymer. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

of the chains, which is now possible because of their increased mobility. Latent heat of crystallization is being given off, meaning that less heat has to be added to bring about a given change in temperature. This has the effect of greatly decreasing the apparent heat capacity. After crystallization is complete, the specific heat increases slightly until melting starts. The apparent specific heat then increases dramatically because a portion of the heat being added to the polymer goes into melting some of the crystallites. After melting is complete, the specific heat again decreases to a value typical of amorphous polymers.

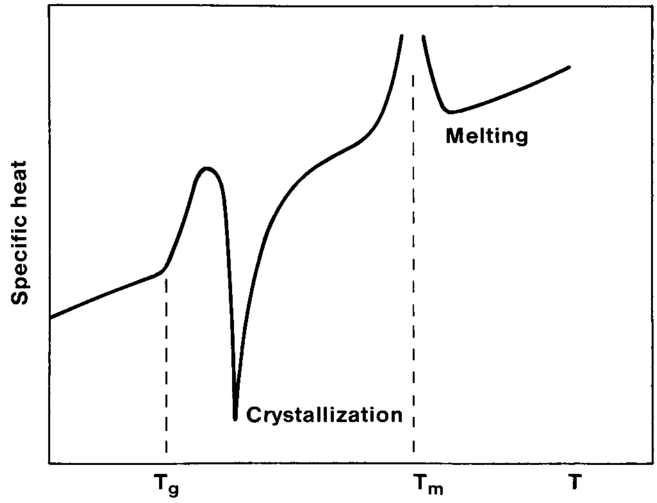


Figure 2.36 Calorimetry results obtained in a bomb calorimeter. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

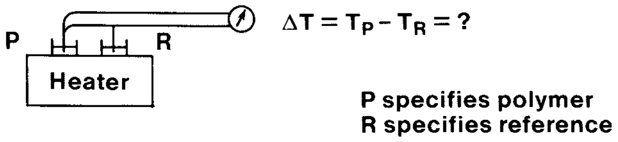


Figure 2.37 Differential thermal analysis (DTA) equipment. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

Differential Thermal Analysis

One of the simpler ways to obtain such information is called differential thermal analysis (DTA), and a typical apparatus is described in Figure 2.37. Basically, the polymer sample P and an inert reference material R are heated from the same source. Thermocouples measure the temperature of the polymer and that of the reference, and the temperature difference $\Delta T = T_P - T_R$ is then plotted as a function of the temperature of the polymer.

Typical results are shown in Figure 2.38. As the temperature is increased, ΔT stays relatively constant until the glass-transition temperature is reached. Then ΔT shifts downward; the temperature of the polymer has decreased because its specific heat has increased from the freeing of some of the molecular motions. The subsequent sharp upward peak in ΔT is due to crystallization, and the downward peak is a consequence of subsequent melting.

Differential Scanning Calorimetry

A similar, simplified technique called differential scanning calorimetry (DSC) is described in Figure 2.39. In this approach, there are *separate* heating elements for the

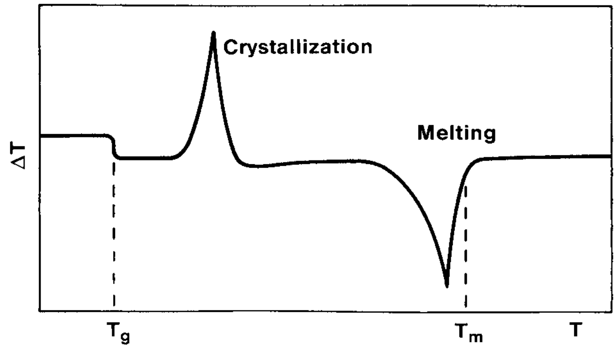


Figure 2.38 Typical DTA results. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

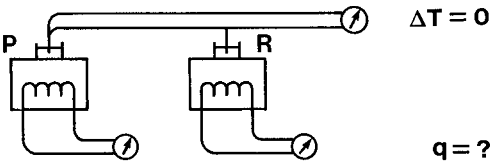


Figure 2.39 Differential scanning calorimetry (DSC) apparatus. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

polymer and the reference material. The currents Q flowing into the two heating elements are adjusted to keep the temperature difference ΔT at zero. Changes in the difference in current ΔQ are then used to locate the transitions. Values of ΔQ can also be used directly to obtain the heat of fusion of the polymer.

Some Other Techniques

Another type of calorimetric technique is called thermogravimetric analysis (TGA). It is the study of the weight of a material as a function of temperature. The method is used to evaluate the thermal stability from the weight loss caused by loss of volatile species. A final example, thermomechanical analysis (TMA), focuses on mechanical properties such as modulus or impact strength as a function of temperature. Both types of analysis are essential for the evaluation of polymers that to be used at high temperatures.

2.7.5 Crystallization and Melting

Thermodynamics

For crystallization to occur, the Gibbs free energy of the system must decrease, as shown in the equation

$$\Delta G_{T,p} = \Delta H - T\Delta S < 0 \tag{33}$$

This leads to the inequality

$$T < \Delta H/\Delta S = T_{\mathrm{m}} \tag{34}$$

which is the obvious requirement that the temperature has to be below the melting point for crystallization to occur. Thus, in the temperature range above T_{m}, crystallization is thermodynamically forbidden. Below T_{m} but not too close to T_{g}, crystallization can occur at a significant rate. However, near and below T_{g}, the chain motions are too sluggish for crystallization to occur. This can be very important if attempts are made to crystallize a polymer. Lowering the temperature too much introduces a kinetic complication: at temperatures close to T_{g} the chains should crystallize for thermodynamic reasons but cannot do so because of the very high viscosity of the medium. When this occurs, the polymer is said to be "quenched."

Annealing of Polymers

There is a rule of thumb that says that the temperature T_{max} for maximum rate of crystallization is given by

$$T_{max} = T_g + (2/3)(T_m - T_g) \tag{35}$$

That is, measured from the T_g, it should be approximately 2/3 the temperature span between the glass-transition temperature to the melting point. Predicted values are generally in sufficiently good agreement with theory to provide useful guidance for the development of annealing procedures carried out to develop crystallinity in a polymer.

Strain-Induced Crystallization

The effect of stretching on the melting point of a polymer is shown in Figures 2.40 and 2.41. The upper sketch in Figure 2.40 shows the usual melting process for chains that can collapse into random-coil configurations. As illustrated in the lower sketch, keeping the chains stretched by mechanical tension prevents their collapse into random coils on melting. This decreases their entropy of fusion and therefore increases their melting point. In a sense, the strain "induces" the crystallization by elevating the melting point. The force acts as a mechanical equivalent of the structural changes already mentioned, where the configurational entropy of a polymer was also decreased, but by the introduction of stiffening groups into the chain backbone.

The melting points of two polymers are shown as a function of elongation in Figure 2.41. An elastomer, such as "inorganic rubber," has a normal melting point T_m below room temperature. However, stretching it increases its melting point to above room temperature. The polymer is now supercooled, and crystallization can occur. This can be very important since crystallites reinforce an elastomer, and thereby improve its mechanical properties. However, following removal of the stretching force, the melting point falls to its original value and the crystallites melt. The stress–temperature results for "inorganic rubber" networks presented in Figure 2.42 illustrate this type of reinforcement.[73]

A similar elevation of the melting point occurs for a polymer that has its normal melting point already above room temperature. An example would be a fibrous material such as one of the Nylons. Stretching such a polymer can induce additional crystallization (and better orient the crystallites), but the crystallization is not lost on removal of the stretching force. This is also illustrated in Figure 2.41.

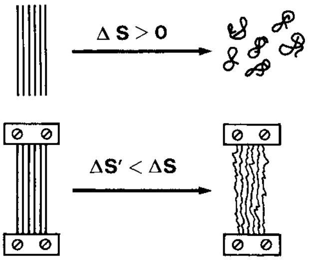


Figure 2.40 Effect of stretching on the melting point $T_m = \Delta H_m/\Delta S_m$. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

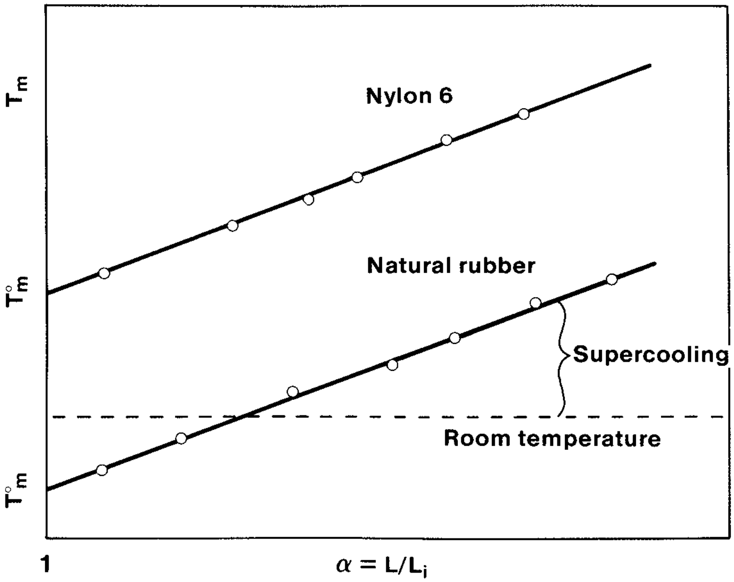
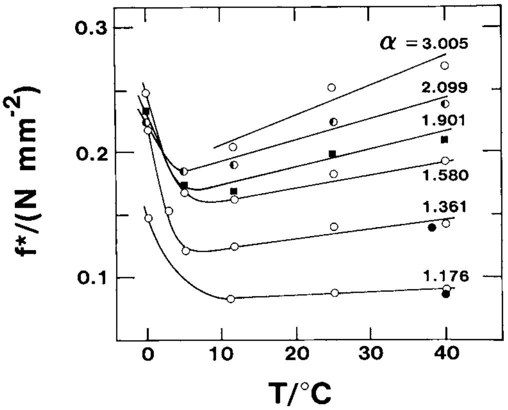


Figure 2.41 Effect of elongation α on high-melting fibers and low-melting elastomers. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

Polymer-Diluent Systems

The addition of a diluent to a crystalline polymer depresses its melting point, as is shown schematically in Figure 2.43. The upper sketch again shows the standard reference case. In the lower sketch, solvent molecules are available to mix with the polymer chains once they separate from the crystalline lattice. The final state is now a polymer solution, instead of a molten polymer. This additional disordering greatly increases the entropy change for the process and therefore decreases the melting point, frequently to the extent of 40–50 °C.

Figure 2.42 Stress–temperature data on "inorganic rubber," in which the upturns in the stress at low temperatures illustrate the reinforcing effects of strain-induced crystallization.[73] Reproduced by permission of Pergamon Press.



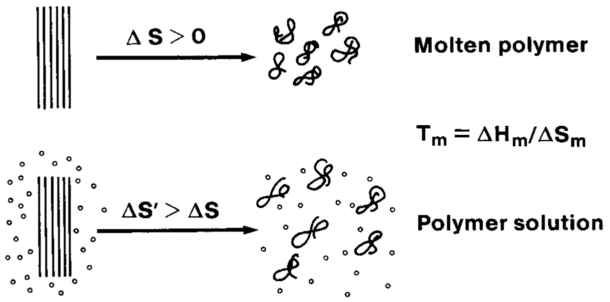


Figure 2.43 Mechanism for the solvent-induced depression of the melting point. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

Application of the Flory–Huggins theory to the melting point depression gives the relationship[1]

$$\left(1/T_{\mathrm{m}} - 1/T_{m}^{0}\right)/v_1 = \left(R/\Delta H_{\mathrm{m}}\right)\left(V_2/V_1\right) - \left(R/\Delta H_{\mathrm{m}}\right)\left(V_2/V_1\right)\chi_1 v_1 \qquad (36)$$

where the Ts are melting points, v_1 the volume fraction of solvent, and the Vs molar volumes. As already mentioned, the temperatures and the heat of fusion ΔH_{m} do not depend on the amount of crystalline material present, and therefore pertain to the 100% crystalline material.

The entropy of fusion can be calculated from the equation

$$\Delta S_{\mathrm{m}} = \Delta H_{\mathrm{m}}/T_{\mathrm{m}}^{0} \qquad (37)$$

and is frequently used as a direct measure of the flexibility of a chain.

Melting-point-depression data plotted in accordance with the above equation are shown schematically in Figure 2.44. The intercept gives the heat of fusion, and the slope gives the thermodynamic interaction parameter χ_1.

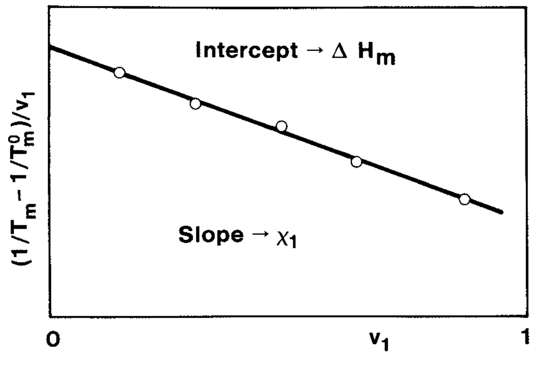


Figure 2.44 Typical melting-point depression data. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

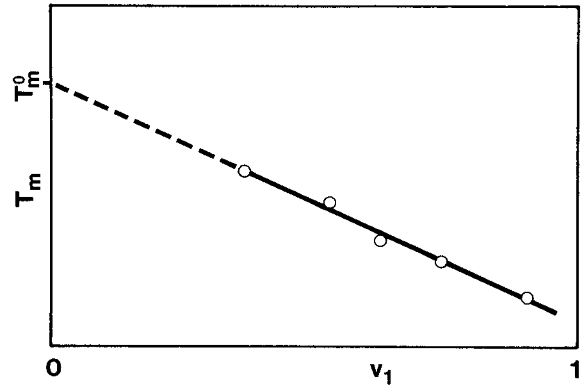


Figure 2.45 Extrapolation of melting-point depression data to estimate the melting point of a polymer that degrades before it melts. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

The melting-point-depression method can also be used to estimate melting points of polymers that degrade before they melt. The depressed melting points are simply plotted against the volume fraction v_1 of solvent in the solution, and extrapolated to the point where v_1 equals zero. The method, illustrated in Figure 2.45, has been used for a variety of polymers, particularly for cellulosic materials.

2.8 Spectroscopy

The discussion of spectroscopic studies of polymers is relatively brief, in part because most of the uses are very similar to well-known, small-molecule applications.

2.8.1 Infrared (IR) and Ultraviolet (UV) Spectroscopy

The following applications are typical of those important in the field of polymers.[74–76] The identification of unknown polymers proceeds through an analysis to identify various functional groups, as does the estimation of the ratios of comonomers, end groups, unsaturation, and impurities. Studies of the chemical reactions of polymers are based on either the disappearance of one type of group or the appearance of another. An example would be the appearance of carbonyl absorption bands in an oxidized hydrocarbon polymer such as polyethylene. Stereochemical structure can also be studied by IR or UV spectroscopy, although this is normally accomplished by nuclear magnetic resonance (NMR) spectroscopy. Finally, IR spectroscopy can be used to determine both the degree of crystallinity and the degree of chain orientation in a polymer.

2.8.2 NMR Spectroscopy

Illustrative applications include the determination of stereochemical structure, and conformational preferences.[77–79] Another application is the determination of chemical composition and chemical sequence distributions in copolymers. A final example is the study of relaxation processes and molecular motions in general, including the determination of transition temperatures from changes in resonance line widths.

2.8.3 Electron Paramagnetic Resonance (EPR) Spectroscopy

EPR spectroscopy is also frequently used in polymer science. Applications involve the detection of free radicals in cross-linking, high-energy irradiation, photochemical degradation and oxidation, and mechanical fracture of polymer chains.

2.9 Mechanical Properties

This section contains two primary topics. The first is polymer rheology, which is concerned with how polymeric materials flow when they are placed under stress. Also of interest are the mechanical properties of polymers, particularly their elasticity. The combination of viscous effects with elastic phenomena is called viscoelasticity.

2.9.1 Elasticity

Continuous Extension

Figure 2.46 shows a stress–strain curve obtained for a typical partially crystalline, uncross-linked polymer, during elongation in the vicinity of room temperature. The data are typically taken on an Instron Tester, and no attempt is made to reach mechanical equilibrium. In this experiment, a strip of the polymer is mounted between two clamps which move apart at a constant rate. A typical rate would be 100% per minute which means that after one minute, a sample originally one centimeter long would increase to two centimeters. The *strain*, or relative length of the sample, is given the symbol γ, and is plotted along the abscissa. The *stress* is given the symbol s and is taken to be the force per unit undeformed cross-sectional area (for examples Newtons mm^{-2}). Stress is shown plotted along the ordinate.

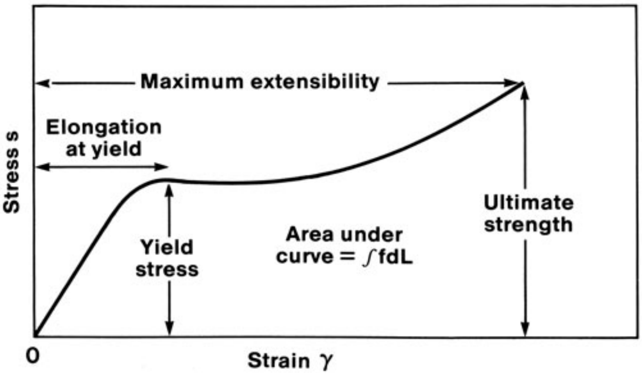


Figure 2.46 Typical non-equilibrium stress–strain curve in elongation. After F. W. Billmeyer, Jr., *Textbook of Polymer Science*, 2nd Ed., Wiley-Interscience, New York, 1971. Reproduced by permission of John Wiley and Sons.

The ratio of any value of the stress to the corresponding value of the strain is called the *modulus*. It is a direct measure of a material's resistance to deformation. Only in the low-strain region of the curve are the stress and strain directly proportional to one another. Therefore, only in this region is the modulus a constant.

When the strain reaches a value called the "elongation at yield," the curve becomes very non-linear. The stress at this point, the "yield stress" is sufficiently high to move the crystallites around in their very viscous surroundings, and to cause them to melt and then recrystallize in new orientations that partly relieve the stress.

The curve then increases monotonically until rupture occurs. The strain at this point is called the "maximum extensibility" and the stress the "ultimate strength." The area under the curve up to the rupture point is also of interest. It corresponds to the integral of fdL, and is therefore the work or energy required for rupture. It is the standard measure of toughness. The larger the area, the tougher the material.

Curves for typical polymeric materials are shown in Figure 2.47. The first is for a soft and weak material, such as an unfilled silicone rubber. "Soft" refers to the fact that the initial slope is small which means a low value of the modulus. "Weak" refers to the low value of the ultimate strength. One does not have to be very strong to pull it apart.

The next type is hard and brittle, for example polystyrene. "Hard" refers to the fact that the initial slope and modulus are large, and "brittle" is another way of saying the maximum extensibility is very small.

These first two materials do not have large areas under their curves, and are therefore not very tough.

The curve shown by a soft and strong material like natural rubber is shown next. The small initial slope and modulus show the material to be soft. At higher elongations, however, strain-induced crystallization occurs and this reinforces the elastomer. As a result its ultimate strength is large and it is therefore quite strong. In other words, one has to be strong to pull it apart.

The fourth example chosen is hard and strong, characteristics shown by many of the Nylons. The hardness is demonstrated by the high initial slope and modulus and the strength by the large value of the ultimate strength.

Soft and tough might refer to one of the new thermoplastic elastomers. The initial modulus could be quite small, but high extensibility would give a large area under the curve. The high degree of toughness means it would take a lot of work or energy to cause it to rupture.

Polymers that are both hard and tough are exemplified by some of the polycarbonates. The high values of the ultimate strength and maximum extensibility combine to give unusually large areas under the curve, and thus considerable toughness.

Hookean Elasticity

The simplest type of elasticity, Hookean elasticity, is defined by the equation

$$s/\gamma = \text{constant} = G \tag{38}$$

A polymer is said to exhibit Hookean elasticity if the ratio of stress to strain is a constant. In this case, the ratio is called "Young's modulus," and is given the symbol G.

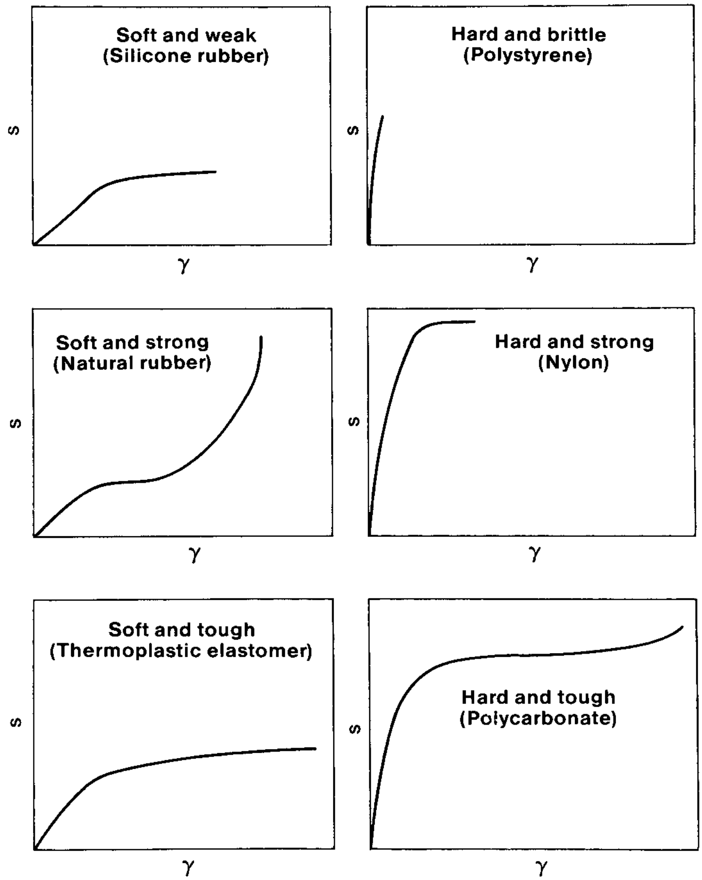


Figure 2.47 Non-equilibrium stress–strain curves for some types of polymers. After F. W. Billmeyer, Jr., *Textbook of Polymer Science*, 2nd Ed., Wiley-Interscience, New York, 1971. Reproduced by permission of John Wiley and Sons.

Rubber-Like Elasticity

A good operational definition of rubber-like elasticity is high deformability with essentially complete recoverability.[80–84] The high deformability can be remarkably high, with some rubbery materials extending up to 15 times their original lengths.

In the simplest molecular theory now available, there are two major assumptions. The first is that *inter*molecular interactions are unimportant, that is, they do not change with deformation. The second is that the deformation is "affine," which means that the molecular deformation is the same as the macroscopic deformation. More precisely, the assumption is that the cross-link positions vary in a simple linear manner with the macroscopic dimensions.

The results for elongation given by the simplest theory are embodied in what is called an *equation of state*, that is, an equation that inter-relates the properties required

to characterize the system. It is given by

$$f^* \equiv f/A^* = \upsilon kT\left(\alpha - \alpha^{-2}\right) \tag{39}$$

where f^* is the nominal stress, f the equilibrium force, A^* the undeformed cross-sectional area, υ the number of density of network chains, k the Boltzmann constant, T the absolute temperature, and $\alpha = L/L_i$ the elongation or relative length of the sample.

This equation is very similar to the ideal gas law, given by

$$p = NkT\left(1/V\right) \tag{40}$$

where p is the pressure of the gas, N the number of gas molecules, and V the volume of the sample. In the case of the gas, the deformation, $1/V$, is simpler than the strain function $(\alpha - \alpha^{-2})$. The α^{-2} term comes from the fact that elongation occur at essentially constant volume, so that the width and thickness of the sample must decrease proportionally as the length increases. This causes some of the chains to be compressed instead of elongated, and the compression is the origin of the subtractive α^{-2} term.

In general, the force is not directly proportional to the absolute temperature, as specified by equation (39). A more refined molecular theory permits the use of precise force-temperature or thermoelastic data to determine the energy change ΔE resulting from the deformation.

Theory also predicts the reduced stress or modulus $[f^*]$, defined as the ratio of the nominal stress to the strain function $(\alpha - \alpha^{-2})$, to be independent of the elongation α. Experimentally, however, the modulus is found to change with α, generally decreasing linearly with decreasing reciprocal elongation.

For this reason, stress–strain isotherms are frequently represented by the semi-empirical Mooney–Rivlin relationship[81,85]

$$[f^*] = 2C_1 + 2C_2\alpha^{-1} \tag{41}$$

where $2C_1$ and $2C_2$ are constants. In the most recent theories, the constant $2C_2$ is considered to be due to the deformation becoming increasingly non-affine as the elongation increases.

2.9.2 Viscosity

The viscosity η of a fluid may be defined by the equation

$$s = \eta \frac{d\gamma}{dt} = \eta\dot{\gamma} \tag{42}$$

where s is the force per unit area required to impart a rate of deformation or rate of shear $\dot{\gamma} = d\gamma/dt$ to the fluid.

In the case of a fluid, the deformation γ itself is not important since a fluid (by definition) will flow to take the shape of the vessel that contains it. Only the time derivative of γ is important, and this quantity, also called the rate of flow or the rate of shear, is represented by the symbol $\dot{\gamma}$.

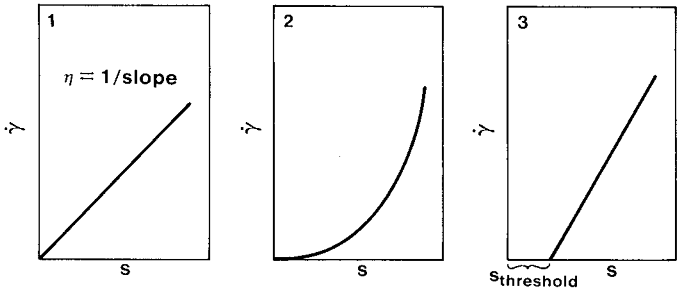


Figure 2.48 Newtonian (1), non-Newtonian (2), and retarded flow (3), where $\dot{\gamma}$ is the rate of flow, s the stress, and η the viscosity. After F. W. Billmeyer, Jr., *Textbook of Polymer Science,* 2nd Ed., Wiley-Interscience, New York, 1971. Reproduced by permission of John Wiley and Sons.

If a shearing stress s gives rise to a rate of deformation $\dot{\gamma}$, then the proportionality factor is called the viscosity η. If this factor is a constant then the flow is said to be "Newtonian"; if not, it is non-Newtonian.

These two types of viscous flow are illustrated in the first two sketches of Figure 2.48, where the reciprocal of the slope of the curve gives the viscosity. In the first sketch the slope and viscosity are constant, so the fluid is Newtonian. In the second sketch the viscosity starts out high (low slope) and then decreases significantly as the stress increases. This type of behavior is shown by liquids that have a temporary gel-like structure. "Non-drip" paints are in this category. The shearing by the paint brush breaks up the structure long enough to get the paint onto the surface. Once the brush is removed, the network sets again and the paint can no longer flow. Retarded flow, illustrated in the third sketch, is just an extreme case of type 2 behavior. The viscosity is infinite (zero slope) until a threshold value of the stress is reached. The flow that occurs after this point can be either Newtonian, as illustrated, or non-Newtonian.

2.9.3 Viscoelasticity

With the above information, it becomes possible to combine viscous characteristics with elastic characteristics to describe the viscoelasticity of polymeric materials.[86–90] The two simplest ways of combining these features are shown in Figure 2.49, where a spring having a modulus G models the elastic response. The viscous response is modelled by what is called a "dashpot." It consists of a piston moving in a cylinder containing a viscous fluid of viscosity η. If a downward force is applied to the cylinder, more fluid flows into it, whereas an upward force causes some of the fluid to flow out. The flow is retarded because of the high viscosity and this element thus models the retarded movement and flow of polymer chains.

The combination of spring and dashpot in series is called the Maxwell model, and was in fact first investigated by the same Maxwell famous for his work on gases and molecular statistics. It is used to model the viscoelastic behavior of uncross-linked polymers. The spring is used to describe the recoverability of the chains that are elongated, and the dashpot the permanent deformation or creep (resulting from the uncross-linked chains irreversibly sliding by one another).

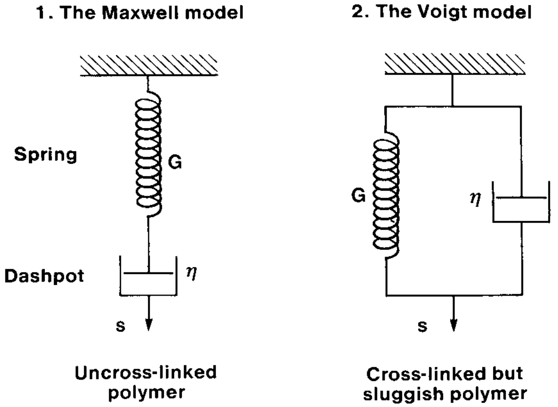


Figure 2.49 Two viscoelasticity models. After F. W. Billmeyer, Jr., *Textbook of Polymer Science*, 2nd Ed., Wiley-Interscience, New York, 1971. Reproduced by permission of John Wiley and Sons.

The parallel arrangement, also shown in Figure 2.49, is called the Voigt model. It is used to model the behavior of a cross-linked but sluggish polymer, such as one of the polyacrylates. Since the spring and dashpot must move in parallel, both the deformation and the recoverability are retarded.

The general differential equation which describes the Maxwell model is

$$\dot{\gamma} = s/\eta + (1/G)(\mathrm{d}s/\mathrm{d}t) \tag{43}$$

with the two terms on the right-hand side coming simply from the defining relationships for the viscosity and modulus. In physical terms, it says that the flow of the polymer has two simply additive parts. The first is from the movement of the chains, and the second is from the effect of a changing stress on the elastic part of the deformation. This equation does not have a general solution, but it can be solved for the two situations of interest to polymer chemists, namely stress relaxation and creep.

The stress-relaxation experiment, described in Figure 2.50, involves stretching the uncross-linked sample to a length L and then measuring the force as it decreases at this constant length as a consequence of the polymer chains undergoing slippage past each other. Because the length is constant, $\dot{\gamma}$ is zero; this simplifies equation (43) in that the

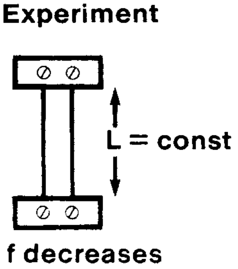


Figure 2.50 The stress-relaxation experiment. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

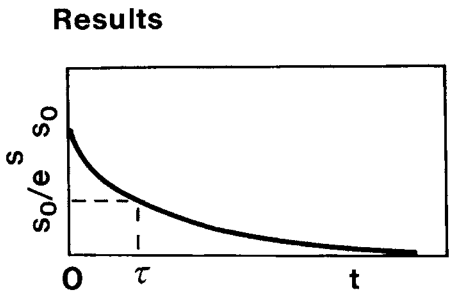


Figure 2.51 Typical stress-relaxation results, where τ is the relaxation time. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

left-hand side disappears. The solution to this equation is

$$s = s_0 e^{-t/\tau} \tag{44}$$

where s_0 is the stress at the initial $t = 0$ and $\tau = \eta/G$ is the relaxation time (the time required for the deformation to decrease to $1/e$ of its original value).

A plot of equation (44), including the definition of the relaxation time, is shown in Figure 2.51. As can be seen, the stress eventually declines to zero if the chains have enough time to undergo the required amount of slippage.

The application of the same Maxwell model to creep data is described in Figures 2.52 and 2.53. As shown in Figure 2.52, the force on the sample is fixed by suspending a constant weight at the end of the sample. The length of the sample is then measured as a function of time. Since the force is constant, $ds/dt = 0$ and the general differential equation again simplifies to a solvable form, namely

$$\dot{\gamma} = d\gamma/dt = s/\eta \tag{45}$$

Its solution is

$$\gamma = (s/\eta)t \tag{46}$$

and states that the deformation increases linearly with time, without limit, and that the proportionality constant is the ratio of stress to viscosity. Plots of equation (46) are

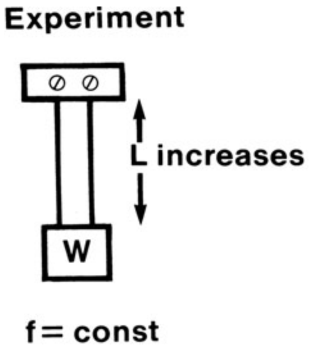
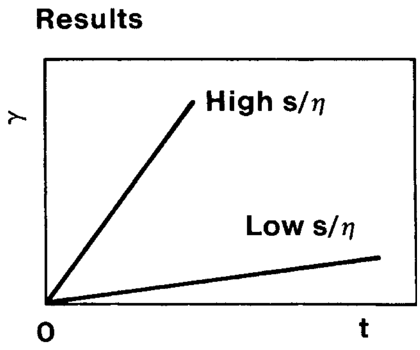


Figure 2.52 The creep experiment. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

Figure 2.53 Typical creep results either for two polymers having different viscosities η, or the same polymer under two different stresses *s*. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.



shown schematically in Figure 2.53. A high slope means that the sample pulls apart rapidly, and this takes place when s/η is large. Thus, this occurs when the stress on the sample is high, or when the viscosity of the polymer is low. The process is slower when s/η is low, that is, when the stress is small or the viscosity of the sample is high.

The use of the Voigt model to characterize cross-linked but sluggish polymers is illustrated in Figure 2.54. As shown by the corresponding equation in this case,

$$s = G\gamma + \eta\dot{\gamma} \tag{47}$$

and this arises because the stress is partitioned between the two parallel arms of the model. The first term comes from the definition of the modulus of the spring, and the second from the definition of the viscosity of the polymer. This differential equation has a general solution, which is given by

$$\gamma = (s/G)(1 - e^{-t/\tau}) \tag{48}$$

when $t = 0$, the exponential is unity and the deformation γ is zero. When t goes to infinity, the exponential is zero, and the deformation reaches its maximum value, specifically the value s/G dictated by the values of the stress and the modulus of the spring.

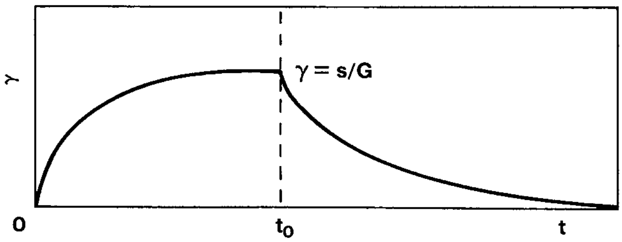


Figure 2.54 Stress–time behavior of a cross-linked but sluggish elastomer. Reprinted with permission from J. E. Mark, "Physical Chemistry of Polymers," ACS Audio Course C-89, American Chemical Society, Washington, DC, 1986. Copyright 1986, American Chemical Society.

Removal of the stress makes the left-hand side of equation (47) zero. This simplified equation can be solved to show how the deformation decreases back to zero. The solution is given by

$$\gamma = \gamma_0 e^{-t/\tau} \tag{49}$$

where γ_0 is the deformation immediately after removal of the stress s. The sketch in Figure 2.54 shows the asymptotic increase in deformation given by equation (48), followed by the asymptotic decrease given by equation (49).

In this general approach to viscoelasticity, appropriate models are constructed for the interpretation of the stress–strain–time behavior of a polymer. Then, values of Young's modulus G of the elastic elements and the viscosities η of the viscous elements are used to characterize and predict the general behavior of the material.

Such analyses are essential in the design of polymeric materials that have predictable mechanical properties.

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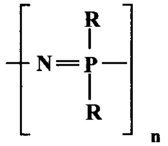
3

Polyphosphazenes

3.1 Introduction

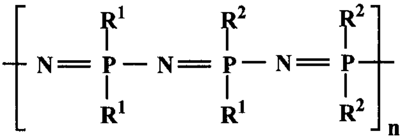
Polyphosphazenes comprise by far the largest class of inorganic macromolecules. At least 700 different polymers of this type have been synthesized, with a range of physical and chemical properties that rivals that known hitherto only for synthetic organic macromolecules.[1]

Most polyphosphazenes have the general molecular structure shown in **3.1**. The polymer backbone consists of alternating phosphorus and nitrogen atoms, with two side groups, R, being attached to each phosphorus. The side groups may be organic, organometallic, or inorganic units. Each macromolecule typically contains from 100 to 15,000 or more repeating units linked end to end, which means that (depending on the organic side groups) the highest molecular weights are in the range of 2 million to 10 million. The bonding structure in the backbone is formally represented as a series of alternating single and double bonds. However, this formulation is misleading. Structural measurements suggest that all the bonds along the chain are equal or nearly equal in length, but without the extensive conjugation found in organic polyunsaturated materials. This anomaly will be discussed later.



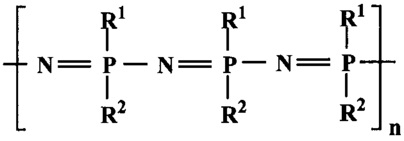
3.1

In addition to linear polyphosphazenes with one type of side group, as shown in **3.1**, other molecular architectures have also been assembled. These include polyphosphazenes in which two or more different side groups, R^1 and R^2, are arrayed along the chain in random, regular, or block distributions (**3.2–3.4**). Other species exist with short phosphazene branches linked to phosphorus atoms in the main chain (**3.5, 3.6**). Also available are macromolecules in which carbon or sulfur replace some of the phosphorus atoms in



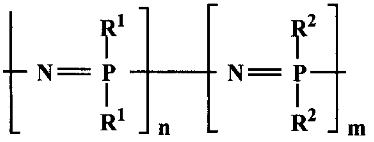
3.2

Random distribution



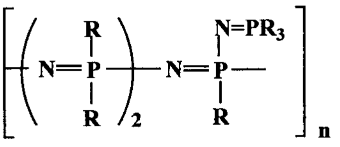
3.3

Non-geminal di-substitution

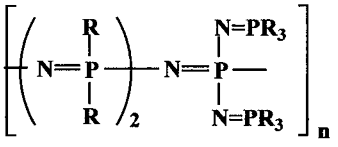


3.4

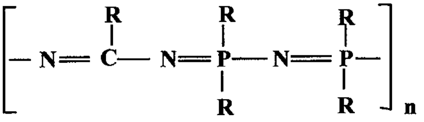
Diblock



3.5



3.6



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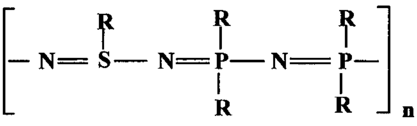
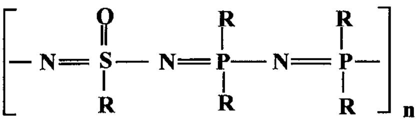


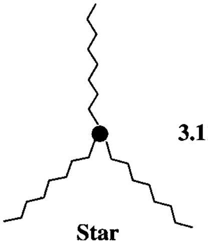
3.8



3.9

the skeleton (**3.7–3.9**). Star-geometry structures (**3.11**), using the symbolism defined by **3.10**, are also accessible. A new and growing area is the field of phosphazene-organic and phosphazene-polysiloxane hybrid linear copolymers (**3.12–3.14**), and comb copolymers of the types shown in **3.15**. In addition, polymers are known in which six-membered phosphazene rings are side groups linked to organic polymers (**3.16**), and where phosphazene rings are linked by organic connector groups to form cyclolinear (**3.17**) or cyclomatrix (**3.18**) materials. It will be clear that this wide range of polymer structures, plus the fact that a wide variety of different size groups can be incorporated into each, makes the polyphosphazene platform one of the broadest in the wide field of polymer chemistry.

Linear polyphosphazene
3.10



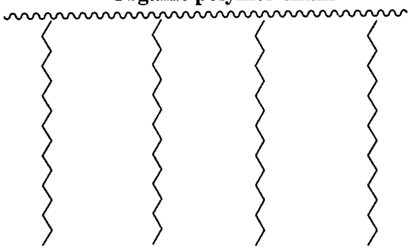
Star
3.11

Phosphazene block **Organic block**
3.12

Triblock 3.13

Triblock 3.14

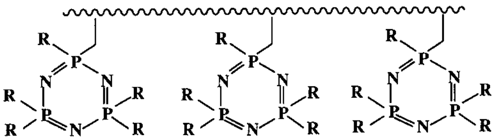
Organic polymer chain



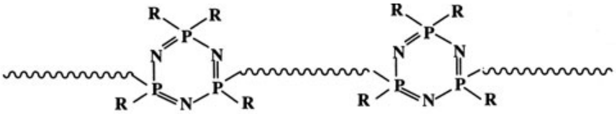
3.15

Polyphosphazene pendent units

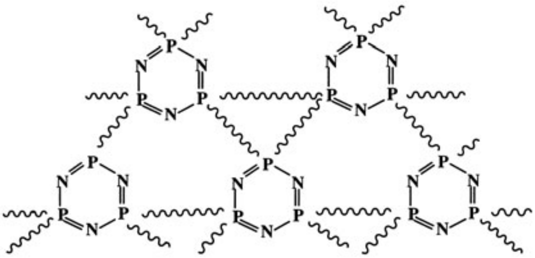
Organic polymer chain



3.16



Cyclolinear
3.17



Cyclomatrix
3.18

Perhaps the most important feature of polyphosphazene chemistry is the unusual method of synthesis that allows the types of side groups, R, to be varied over a very broad range. Different side groups generate different properties such that the characteristics within one type of architecture may vary from those of elastomers to glasses, from water-soluble to hydrophobic polymers, from bioinert to bioactive materials, and from electrical insulators to ionic conductors. This versatility underlies the technological developments that have occurred in this area. For example, certain variants of **3.1** are solvent-resistant elastomers that are used in demanding engineering applications (Figure 3.1). Others are used as fire-resistant, heat-, electrical-, or sound-insulation materials (Figure 3.2). Yet other variations are under development as non-burning textile fibers (Figure 3.3), or as biomaterials, controlled drug delivery systems, hydrogels, membranes, or optical materials.

In the rest of this chapter an attempt will be made to describe how this field developed, how polyphosphazenes are synthesized, how the system provides almost unprecedented opportunities for the design of new macromolecules, and how the molecular structure–property relationships have been developed to produce a wide range of advanced materials.

3.2 History

The origins of this field can be traced back more than 160 years to small molecule inorganic chemistry developed in Europe. For example, Liebig[2] and Rose[3] first reported in 1834 that phosphorus pentachloride reacts with ammonia to form a white, crystalline compound that was soluble in organic solvents. Subsequent work by Gerhardt,[4] Laurent,[5] Gladstone and Holmes,[6] and Wichelhaus[7] established the formula of this

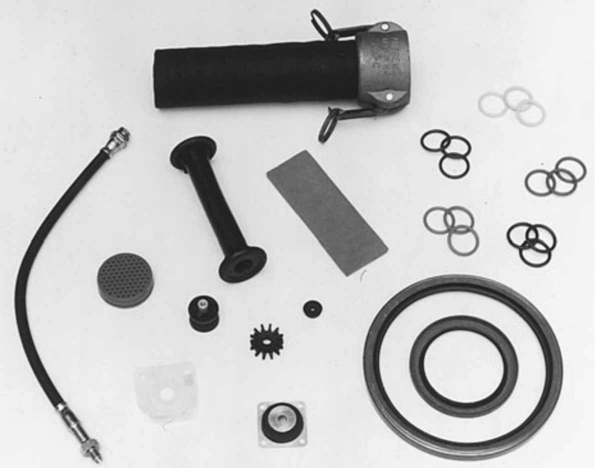
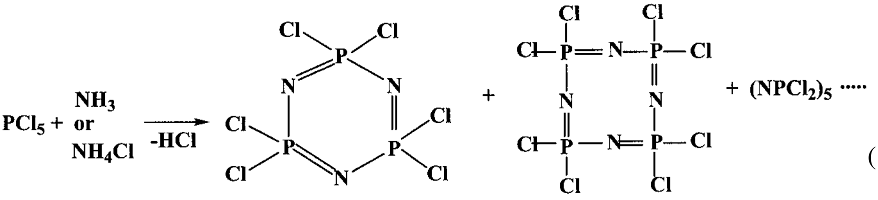


Figure 3.1 Polyphosphazene elastomers of general formula, $[NP(OCH_2CF_3)(OCH_2(CF_2)_x CF_2H)]_n$, fabricated into fuel lines, O-rings, gaskets, and other hydrocarbon-resistant devices. Reproduced by permission of the Firestone Tire and Rubber Company, and Ethyl Corporation.

compound to be $N_3P_3Cl_6$. A corresponding tetramer, $N_4P_4Cl_8$ was also isolated and studied. It was later suggested by the American chemist, H. N. Stokes in 1897, that $N_3P_3Cl_6$ has the cyclic structure shown in **3.19** and that $N_4P_4Cl_8$ has the structure shown in **3.20**.[8–11] He also isolated higher cyclic counterparts such as $(NPCl_2)_{5-7}$. The overall synthesis reaction is shown in reaction (1).



(1)

3.19 **3.20**

Stokes was the first person to prepare a polymeric form of these species. He reported that any of the small-molecule cyclic chlorophosphazene compounds, when heated, were transformed into a rubbery material that was later called "inorganic rubber."[11] This material swelled in organic solvents such as benzene but it did not dissolve. Stokes also described how inorganic rubber decomposed to reform the cyclic compounds when heated to high temperatures under reduced pressure. His accomplishments at that time are all the more remarkable because these compounds are sensitive to a moist atmosphere in which they are hydrolyzed to ammonium phosphate and hydrochloric acid.

It is quite clear from his papers that Stokes recognized that inorganic rubber was a polymer, presumably an extension of the series of cyclic compounds he had isolated. However, it is unlikely that he knew that inorganic rubber was a high polymer with thousands of repeating units linked end to end, since the idea that high polymers could exist was not accepted until Staudinger's work 40 years later. Moreover, the use of inorganic

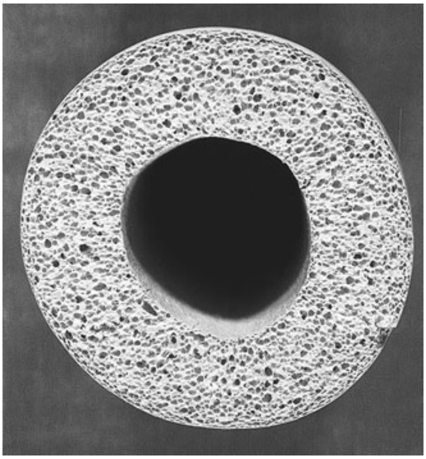


Figure 3.2 Cross section of an expanded foam rubber heat- and sound-insulation tube of a poly(aryloxyphosphazene). Reproduced by permission of Ethyl Corporation.

rubber as a reaction intermediate was not possible because this material was insoluble in all solvents and was hydrolytically unstable. It is now know that inorganic rubber was cross-linked, and the further development of this field would have to await the synthesis of an uncross-linked and therefore soluble form of this polymer.

During the next 40 years inorganic rubber was mentioned sporadically as a laboratory curiosity, but was largely ignored by the mainstream scientists of the day. The slow acceptance of Staudinger's controversial idea[12] that long-chain macromolecules could exist, and the demonstration by Meyer and Mark[13] in the 1920s and 1930s that natural rubber is a linear macromolecule, stimulated a brief resurgence of interest in "inorganic rubber." X-ray diffraction experiments by Meyer, Lotmar, and Pankow[14] in 1936 strongly suggested that

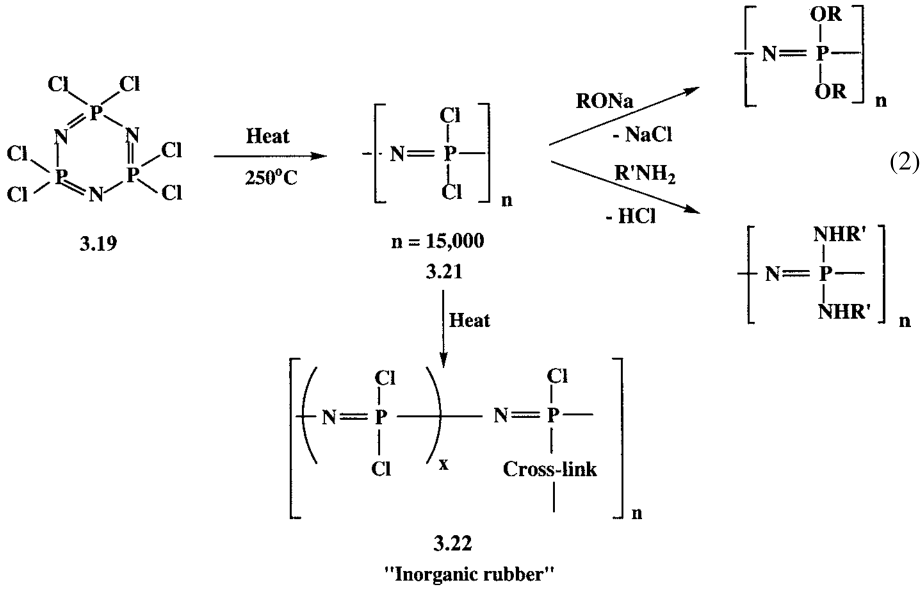
Figure 3.3 Textile fibers of $[NP(OCH_2CF_3)_2]_n$, a non-burning polymer. Reproduced by permission of Ethyl Corporation.

this material contained linear polymeric chains with a repeating unit of the type shown in **3.1**. However, the insolubility of the polymer in all known solvents and its hydrolytic instability in the atmosphere discouraged a more serious interest in this material.

This situation persisted until the mid-1960s when Allcock, Kugel, and Valan[15–17] published a series of three papers that provided the starting point for the modern approach to polyphosphazenes. The theme of these papers was as follows:

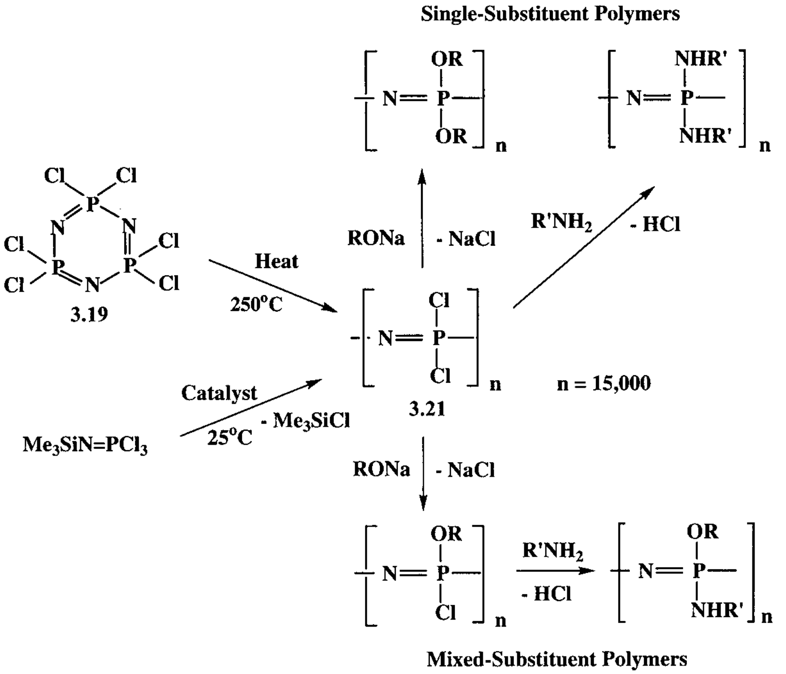
1. The hydrolytic instability of inorganic rubber is an indication of the high reactivity of the phosphorus-chlorine bonds. *Thus, this reactivity might be utilized to replace the chlorine atoms by organic groups to give hydrolytically stable polymers.* In this sense, the polymer might be utilized as a macromolecular intermediate for the synthesis of a range of stable organic derivatives. Early attempts to replace the chlorine atoms in inorganic rubber by alkoxy groups provided encouragement for this idea, but the substitutions were never complete because of the insolubility of the material in all solvents.

2. Thus, the main hurdle to this approach was the insolubility of inorganic rubber, even though it swelled in organic solvents such as benzene. Insolubility but swellability is a characteristic of cross-linked polymers, and it was proposed that the structure of this material is as shown in **3.22**. Therefore, a method was needed to prepare this polymer in the uncross-linked state. This method was found from a careful study of the process by which hexachlorocyclotriphosphazene (**3.19**) is converted to poly(dichlorophosphazene). *Careful control of the time, temperature, and cyclic trimer purity, and termination of the reaction before it reached approximately 70% conversion to polymer, yielded an essentially linear high polymer (3.21) that dissolved completely in organic solvents such as benzene, toluene, or tetrahydrofuran.* However, further heating of this polymer caused cross-linking of the chains and yielded the insoluble inorganic rubber (**3.22**) described by Stokes. The overall sequence is summarized in reaction (2).



(2)

3. When dissolved in a suitable solvent, uncross-linked poly(dichlorophosphazene) (**3.21**) functioned as a remarkable macromolecular reactant (reaction sequence (3)). When treated with organic nucleophiles such as the sodium salts of alcohols or phenols, or with primary or secondary amines, *all the chlorine atoms along the polymer chain could be replaced by organic units.* This is all the more remarkable because an average of 30,000 chlorine atoms per molecule are replaced.



(3)

4. *The derivative polymers proved to be hydrolytically stable and to possess a broad range of unusual, interesting, and useful properties.* Glass-transition and melting temperatures, polymer solubilities, and surface properties varied widely with the presence of different side groups. The polymer backbone was found to be stable to heat and high energy radiation. Even during the early stages of development of this field it was obvious that a broad range of uses could be developed from these polymers. Subsequent developments over the following 35 years have yielded more that 700 different polyphosphazenes with different side groups and different skeletal architectures.

The preparation of uncross-linked poly(dichlorophosphazene) (**3.21**) was the single most important factor in the initial development of polyphosphazene chemistry. Structural diversity in classical organic polymers is achieved by the polymerization of different *monomers.* If a new organic polymer is to be synthesized, a method has to be found for the polymerization of each new monomer, and this is perhaps the greatest challenge in conventional organic polymer chemistry. By contrast, if significant structural and property changes can be made by variations in the substitution chemistry of only one preformed polymer, facile access is provided to a large number of different macromolecules. Unfortunately, very few classical organic polymers have the necessary reactivity to allow this approach to be used. It was the recognition that phosphorus-chlorine bonds are so

much more reactive to nucleophilic attack than the carbon-hydrogen or carbon-chlorine bonds in organic polymers that focussed attention on the possible utility of poly(dichlorophosphazene). Thus, the synthesis of uncross-linked poly(dichlorophosphazene) and the demonstration of its reactivity were the key experiments from which this field radiated.

3.3 Alternative Synthesis Routes to Linear Polymers

3.3.1 Summary of Available Methods

Linear poly(organophosphazenes) are now synthesized by six different methods. These are: (a) The ring-opening polymerization of $(NPCl_2)_3$ mentioned above, followed by macromolecular substitution; (b) Ring-opening polymerization of organic substituted phosphazene cyclic trimers, usually followed by macromolecular substitution; (c) Condensation polymerizations that yield poly(dichlorophosphazene) followed by macromolecular substitution, including the synthesis of block and graft hybrid copolymers; (d) Condensation polymerization of organic-substituted *N*-silylphosphoranimines such as $Me_3SiN\text{-}PR_2Cl$ directly to organo-substituted polymers; (e) Careful decomposition of organophosphorus azides such as R_2PN_3, and (f) Secondary reactions carried out on the organic side groups already present along a polyphosphazene chain. These approaches will be discussed in turn.

3.3.2 The Ring-Opening Polymerization/ Macromolecular Substitution Route

Significance

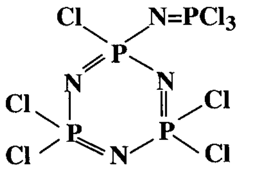
The earliest synthesis method, which involves a ring-opening polymerization of a cyclic chlorophosphazene followed by replacement of the chlorine atoms in the polymer by organic groups, is the most extensively developed route to the preparation of poly(organophosphazenes). It is summarized in reaction sequence (3).

Ring-Opening Polymerization

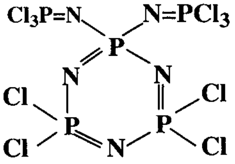
Hexachlorocyclotriphosphazene (**3.19**) is prepared on an industrial scale by the interaction of phosphorus pentachloride with ammonium chloride in an organic solvent such as chlorobenzene. This compound, after careful purification and protection from moisture, is heated in the molten state at temperatures between 210 and 250 °C to induce polymerization.[15–18] The mechanism of this reaction is discussed in a later section. Here it is sufficient to note that the process can also be applied, with minor variations, to cyclic phosphazo-phosphazenes (**3.22a, 3.23**), to cyclic fluorophosphazenes (**3.24, 3.25**), and to cyclic carbo- (**3.26**), thio- (**3.27**), and thionyl (**3.28**) -phosphazenes.

Macromolecular Substitution

Solutions of poly(dichlorophosphazene) (**3.21**) in benzene, toluene, or tetrahydrofuran react rapidly and completely with nucleophiles such as sodium trifluoroethoxide to yield derivative polymers as shown in reaction sequence (3). An impetus for this



3.22a



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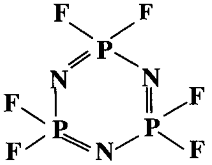

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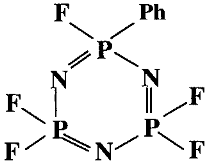
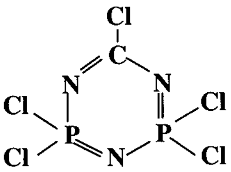
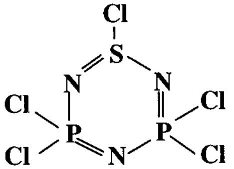


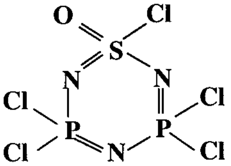
3.25



3.26



3.27



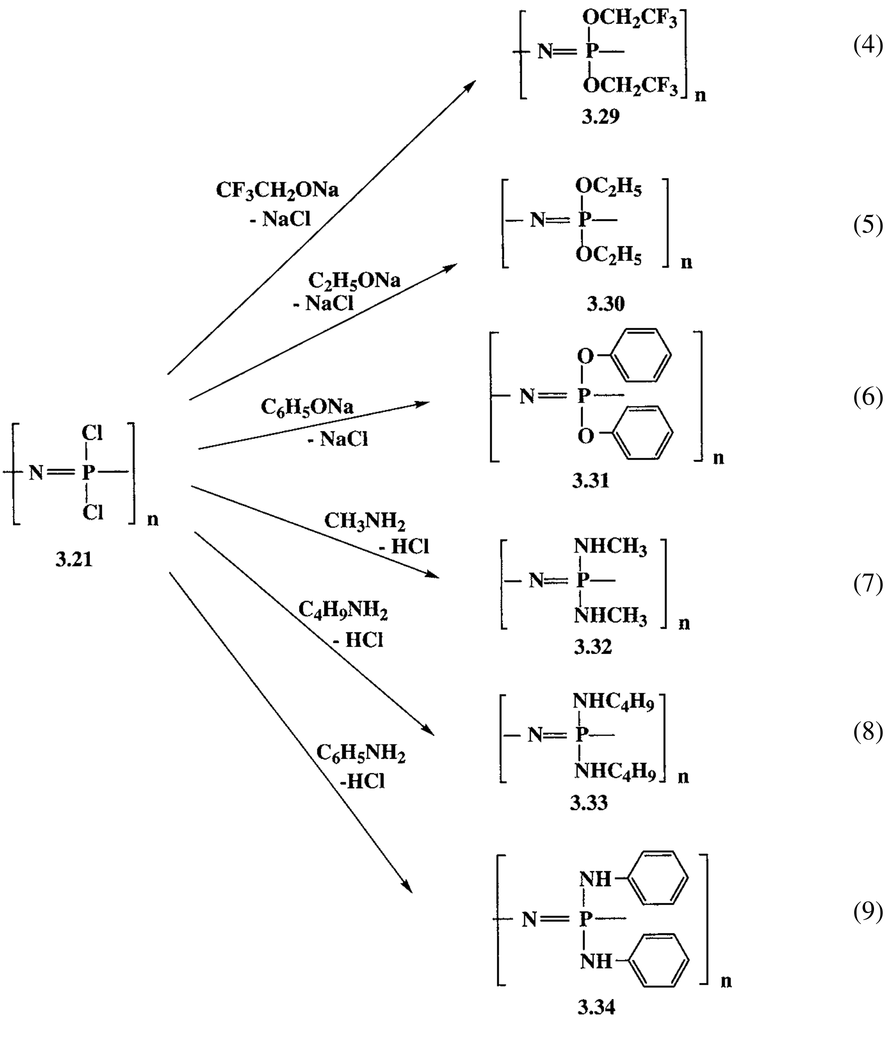
3.28

substitution is the precipitation of sodium chloride from solution, a process that drives the reaction to completion. Example reactions to give single-substituent polymers are shown in reactions (4)–(9). Polymer **3.29**, produced by the reaction of $(NPCl_2)_n$ with sodium trifluoroethoxide, as shown in reaction (4), was the first stable poly(organophosphazene) to be synthesized.[15,16] It is still one of the most interesting (see later). A wide range of other alkoxy or aryloxy groups can be introduced, such as the ethoxy groups in **3.30** or the phenoxy groups in **3.31**.

One of the few limitations to this process is the ability of certain bulky organic side groups to slow the replacement of nearby chlorine atoms by steric hindrance. Hence, the introduction of multi-ring- or ortho-substituted aryloxy units may require forcing (high temperature) conditions in a sealed reactor.

Aminolysis of poly(dichlorophosphazene) also takes place readily to yield poly(aminophosphazenes) such as **3.32**, **3.33**, or **3.34**.[17,18] Here too, steric hindrance effects may slow the replacement of the last 25% of the remaining chlorine atoms, thus requiring forcing conditions toward the end of the reaction.

Inherent in the macromolecular substitution method is the possibilty that two or more different organic groups can be introduced either simultaneously or sequentially to give mixed-substituent polymers. Steric hindrance effects that slow the reaction rate after a bulky side group has been introduced allow the controlled introduction of a



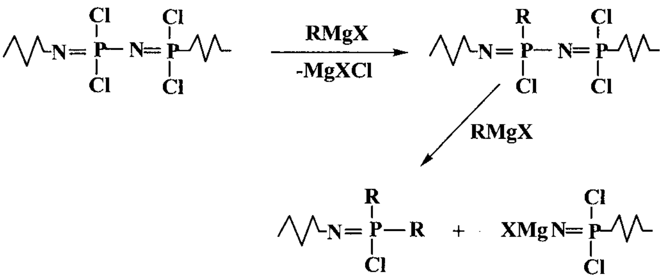
second set of side groups, as shown in reaction sequence (3). Thus, the treatment of $(NPCl_2)_n$ with diethylamine (even in excess) results in the replacement of only one chlorine atom per phosphorus.[18] However, the remaining chlorine atoms can be replaced by treatment with a less-hindered nucleophile such as methylamine, short-chain alkoxides or, in a few cases, with alkyl or aryl organometallic reagents.

This principle can be utilized for a number of different initial nucleophiles. Phenoxy and substituted phenoxy side groups replace less that 100% of the chlorine atoms under mild reaction conditions, but the remaining chlorine atoms react with a less-hindered nucleophile such as trifluoroethoxide.

Mixed-substituent polyphosphazenes are also accessible by utilizing the different reactivities of halogens according to their location in the polymer. For example, the chlorine atoms in the side groups of phosphazo polymers (**3.5** and **3.6**) are more reactive than those linked directly to the main chain: hence, the side-group halogens react first,

leaving the main-chain chlorines to be replaced by a different reagent. Differences in positional reactivity are also found in poly(carbo-, thio-, and thionyl-phosphazenes).

The third pathway involves the interaction of poly(dichlorophosphazene) with organometallic nucleophiles such as Grignard or organolithium reagents. Unlike their oxo- or nitrogen-nucleophile counterparts, organometallic reagents generate more complicated reactions.[19,20] For example, the interactions of $(NPCl_2)_n$ with RMgX or RLi usually follow two concurrent and conflicting pathways. Replacement of chlorine by the group R certainly occurs, but this is accompanied by (or followed by) cleavage of the phosphorus-nitrogen bonds in the skeleton. This sequence of events is summarized in reaction (10).

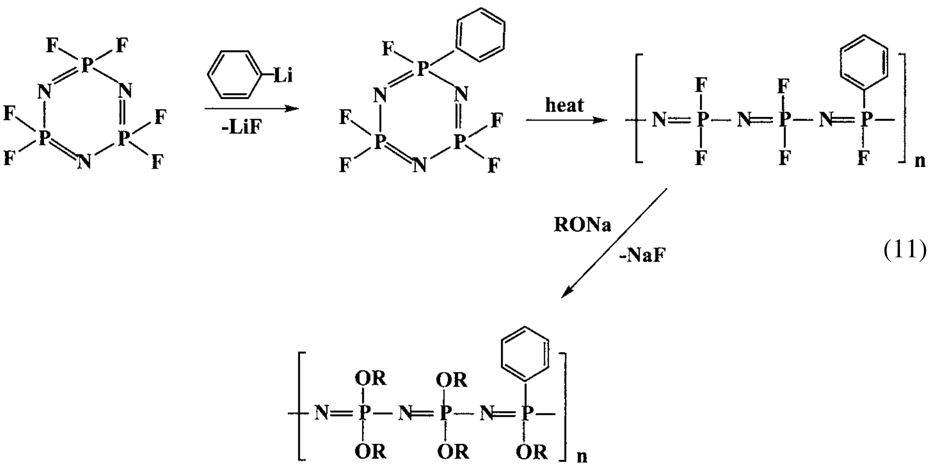


(10)

The skeletal cleavage reaction appears to depend on a coordination of the organometallic molecules to skeletal nitrogen atoms. Thus, any structural feature of the polymer that encourages such coordination will also favor cleavage of the backbone. Ultimately this depends on the lone-pair electrons at nitrogen. Chlorine atoms are excellent electron-withdrawing units: hence, they will lower the density of the lone-pair electrons at skeletal nitrogen. This protects the skeleton against cleavage. But if the chlorine atoms are replaced by alkyl or aryl groups, this protective effect is lost. Thus, as an organometallic substitution reaction proceeds, an increased probability exists that phosphorus-nitrogen bond cleavage will occur rather than halogen replacement.

Because fluorine is a more electron-withdrawing unit than chlorine, it might be expected that fluorophosphazenes might be more resistant to skeletal cleavage than their chlorophosphazene counterparts. This is correct, and is illustrated by the reaction profiles shown in Figure 3.4, which compare the chain lengths of polymers obtained by treatment of the polymers $(NPCl_2)_n$ and $(NPF_2)_n$ with phenyllithium.[20,21] When $(NPCl_2)_n$ is the reaction substrate, phosphorus-nitrogen skeletal cleavage is detectable almost from the start of the reaction. However, chain cleavage is not noticeable with $(NPF_2)_n$ until roughly 75% of the fluorine atoms have been replaced by the organic groups.

Incidentally, $(NPF_2)_n$ is prepared by polymerization of the trimer, $(NPF_2)_3$, which itself is obtained from $(NPCl_2)_3$ by treatment with sodium fluoride. In principle, $(NPF_2)_n$ is a very useful macromolecular intermediate for the reasons just discussed. However, in practice, its insolubility in all solvents except specialized fluorocarbon media limits its usefulness. This problem can be overcome by the use of a fluoro-polymer that has one phenyl side group for every three repeating units (reaction (11)). This macromolecule is soluble in several ordinary organic solvents and is, thus, an excellent substrate for fluorine replacement reactions. The polymer is made by a method described in the following section.



(11)

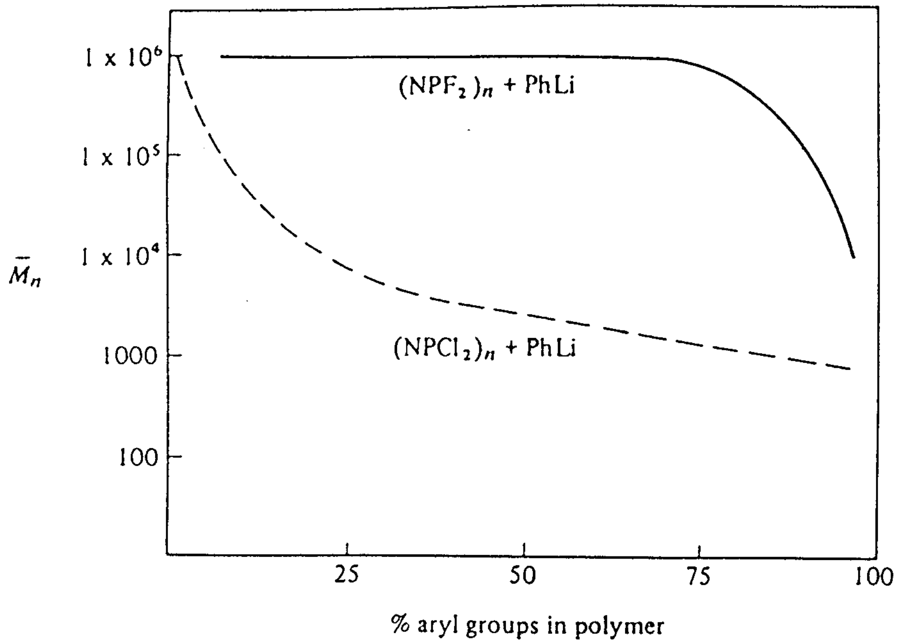


Figure 3.4 Comparison of the variation in average molecular weight for $[NP(C_6H_5)_x(OCH_2CF_3)_y]_n$ versus the percentage of phenyl groups introduced via the reaction of $(NPF_2)_n$ or $(NPCl_2)_n$ with phenyllithuim. The trifluoroethoxy groups were introduced later to facilitate the molecular weight measurements. From references 20 and 21.

One additional technique has been developed to allow organometallic reagents to be used as reactants for the introduction of alkyl, aryl, carboranyl, or transition metal organometallic side groups into chlorophosphazene polymers. If most of the chlorine or fluorine atoms in poly(dichloro- or fluoro-phosphazene) are replaced by electron-withdrawing organic groups, such as trifluoroethoxy units, the remaining chlorine or fluorine side units can be replaced using organometallic reagents without significant skeletal cleavage.[22] This is a useful technique for the preparation of mixed-substituent polymers.

However, in spite of these complications, the overall macromolecular substitution route allows access to an enormous range of different polymeric structures. Moreover, the length of the polymer chain is usually unaffected by the replacement of halogen by organic side groups. Thus, it is possible to alter the side-group structure in polyphosphazenes *without changing any other structural features*, and this is of vital importance for the assessment of structure–property relationships.

3.3.3 Polymerization of Organo- or Organometallo-Substituted Cyclic Phosphazenes

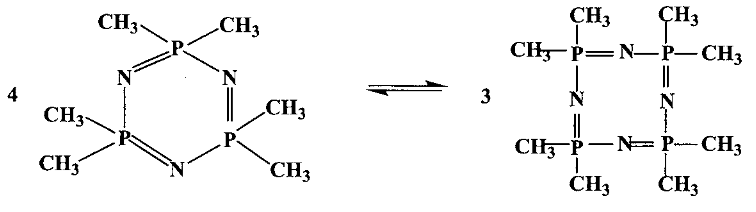
The macromolecular substitution route just described is a powerful method for the synthesis of a broad range of new phosphazene polymers. Yet that approach has limitations if the target polymers are to contain organic side groups linked to the skeleton through carbon-phosphorus bonds. As discussed, organometallic macromolecular substitution reactions allow the introduction of alkyl, aryl, or organometallic groups, but often at the expense of skeletal cleavage or incomplete halogen replacement. The methods discussed in this and a later section provide alternative approaches that avoid the interaction of organometallic reagents with high polymeric phosphazenes.

It is usually easier to carry out organometallic substitution reactions with *small-molecule* chloro- or fluoro cyclic phosphazenes than with the analogous high polymers. For one thing, the consequences of skeletal cleavage reactions are less severe in small molecule chemistry than for high polymers. Consider the following example. Suppose that the interaction of an organometallic reagent (say an organolithium reagent) with a chlorophosphazene results in an average of one skeletal cleavage reaction for every twelve halogen replacement reactions. At the high polymer level this situation would result in a chain cleavage once for every six repeating units along the chain. Thus, the products would on the average be only six repeating units long. These molecules would have none of the properties of high polymers. So the yield of polymer would be zero. On the other hand, the same reaction carried out with a cyclic trimeric phosphazene would cleave the ring of only one molecule out of every two. Hence, the yield of the substituted cyclic phosphazene would be 50%. For this reason it is much easier to prepare organo-substituted small-molecule cyclic trimeric phosphazenes by organometallic substitution chemistry than it is to prepare the analogous high polymers.

Thus, the second approach to the synthesis of poly(organophosphazenes) involves the introduction of the organic (or organometallic) side groups at the cyclic trimer level, followed by ring-opening polymerization of the substituted cyclic trimer to the high polymer (reaction (11)).[23]

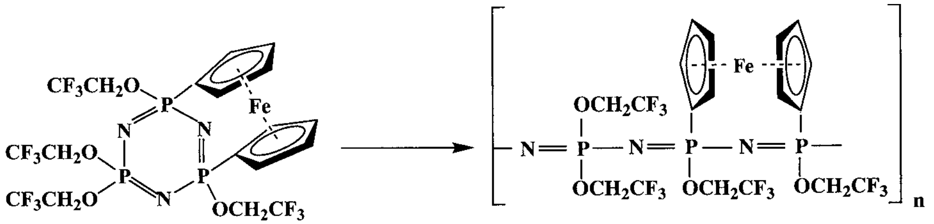
This approach has both advantages and limitations. For example, although cyclic trimers that bear one or two organic or organometallic side groups and five or four

chlorine or fluorine atoms usually polymerize almost as easily as $(NPCl_2)_3$ or $(NPF_2)_3$, the tendency for polymerization declines as more and more halogen atoms in the trimer are replaced by organic groups.[24] For example, as shown in reaction (12), the cyclic trimer that bears six methyl groups, $(NPMe_2)_3$ (**3.35**), undergoes ring-ring equilibration to the eight membered cyclic tetramer (**3.36**) when heated, but it does not polymerize to the high polymer.[25] The same is true if the trimeric ring bears six phenyl groups or six trifluoroethoxy units. Possible reasons for this will be discussed in a later section.



(3.35) (3.36) (12)

However, this restriction does not hold if the phosphazene ring is subjected to ring-strain by the presence of a transannular ferrocenyl group, as in structure **3.37** and reaction (13).[26] Under these circumstances, polymerization takes place to give **3.38** even if no halogen atoms are attached to the phosphorus atoms, although the reaction is accelerated by the presence of catalytic quantities of $(NPCl_2)_3$.

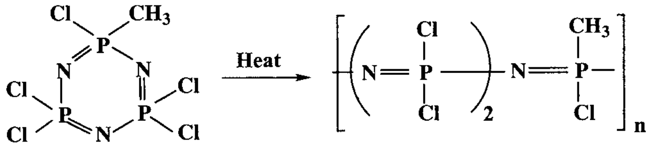


3.37 3.38 (13)

The ring-opening polymerization of organo- or organometallo-substituted cyclic trimeric phosphazenes has been used to prepare a wide range of phosphazene high polymers in which alkyl-,[27,28] aryl-,[24] carboranyl-,[29] metallocenyl-,[30] organosilicon-,[31] or aryloxy-[32] side groups are attached to the chain (see reactions (14)–(16)). Examples of these polymers, and their properties and uses, will be discussed in later sections.

3.3.4 Mechanism of Ring-Opening Polymerizations

It will be clear from the discussion so far that ring-opening polymerization is a crucial step in the synthesis of most polyphosphazenes. Hence, a knowledge of the mechanism of this process is important for widening the scope of this field, optimization of



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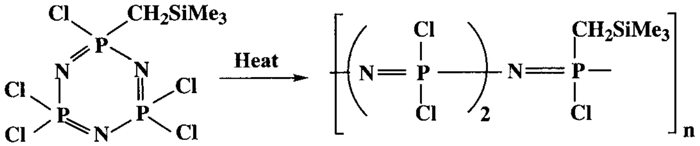

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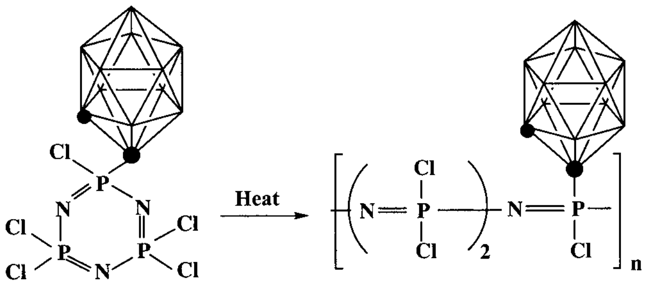


(16)

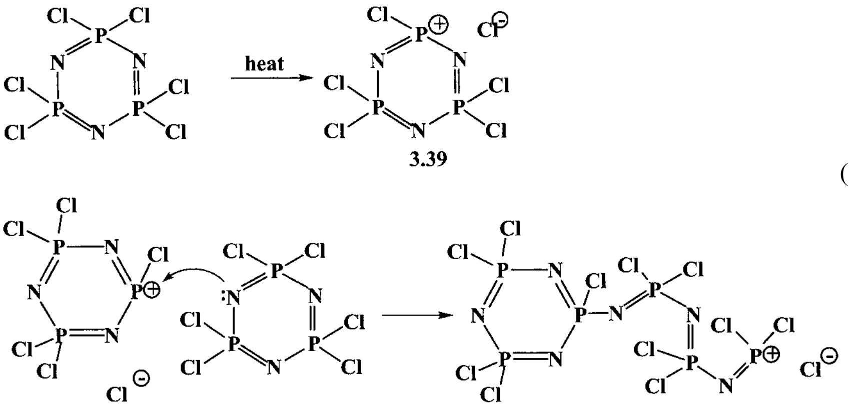
Black circles represent carbon atoms. BH units at other sites.

polymerization conditions, and for scale-up of these processes. Moreover, by understanding the ring-opening mechanism, it may be possible, for example, to induce the polymerization of cyclic trimers, such as $(NPMe_2)_3$ or $(NPPh_2)_3$, that so far have resisted polymerization.

The initial thinking on this topic was focused on the polymerization of $(NPCl_2)_3$, $(NPCl_2)_4$, and the fluoro analogue, $(NPF_2)_3$. The following experimental observations are known.

(1) Polymerization appears to require the presence of several halogen atoms attached to the ring phosphorus atoms. Replacement of all the halogen atoms by methyl, phenyl, or OCH_2CF_3 groups blocks the polymerization process (but not the ring-expansion equilibration).
(2) Ions appear to participate in the polymerization process. The ionic conductivity of molten $(NPCl_2)_3$ remains low until the trimer is heated into the temperature range where polymerization occurs. At this point the conductivity rises dramatically.[33]
(3) Traces of impurities, especially water, BCl_3, or $AlCl_3$ exert a catalytic effect on the polymerization of $(NPCl_2)_3$.[34,35]
(4) The temperature required for the onset of polymerization of $(NPF_2)_3$ (350 °C) is much higher than that required for polymerization of $(NPCl_2)_3$ (210–250 °C).[40–42]

These observations were used as a basis for proposing the polymerization mechanism shown in reaction sequence (17).[33]



3.39

(17)

In this mechanism it is assumed that polymerization is induced by ionic species, such as **3.39**, generated by the ionization of P-Cl bonds to form a cyclic (or linear) phosphazenium ion. The phosphazenium ion would then act as a cationic initiator by attack on the skeletal nitrogen atom of an $(NPCl_2)_3$ molecule, inducing ring opening and chain propagation by a cationic mechanism.

Traces of water might function as a catalyst by assisting the separation of chloride ion, or could serve as co-catalytic species. Boron trichloride, commonly used as a catalyst in the commercial process,[35] would also be expected to promote the separation of Cl^- from phosphorus, and would be stabilized as the BCl_4^- ion. Moreover, this mechanism would explain why $(NPF_2)_3$ requires a higher temperature for polymerization than $(NPCl_2)_3$, since it is generally assumed that more energy is required to thermally cleave a P-F bond than a P-Cl bond. The mechanism would also explain why replacement of all the halogen atoms in $(NPCl_2)_3$ or $(NPF_2)_3$ by organic groups blocks the polymerization process, since it would be exceedingly difficult to induce the thermal ionization of a methyl or phenyl group from phosphorus.

However, this cannot be the complete story. As mentioned earlier, ring strained phosphazenes that lack halogen side groups do polymerize, and organo-substituted trimers undergo ring expansion without forming high polymers. Either two independent mechanisms are involved or another factor entirely must be considered.

Another factor that appears to exert a powerful influence on the ability of a cyclic phosphazene to polymerize is the amount of intramolecular steric hindrance generated by the side groups. Figure 3.5 illustrates that, irrespective of the chain conformation assumed by the high polymer, the side groups are always closer to their neighbors along a chain than they are when attached to a cyclic trimer. Thus, if the groups are large they will interfere with each other and experience more repulsions in the polymer than in the cyclic trimer. Hence, the polymer will be thermodynamically less stable than the cyclic trimer. This means that, even if a polymerization mechanism is accessible, the trimer will not polymerize. The system would be above its "ceiling temperature," the temperature at which a polymer is always thermodynamically unstable relative to small-molecule species.

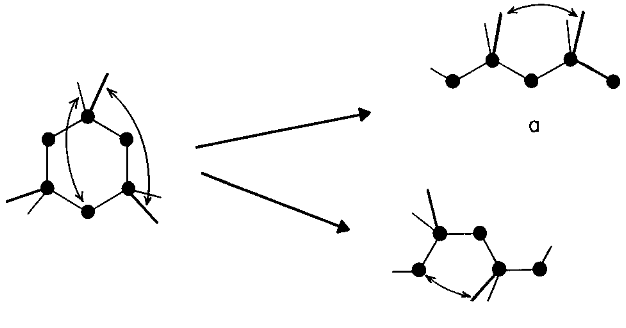


Figure 3.5 Schematic representation of the effect of steric hindrance generated by bulky side groups on a cyclic trimeric and a high polymeric phosphazene. Depolymerization of a high polymer to a cyclic trimer relieves the intramolecular crowding.

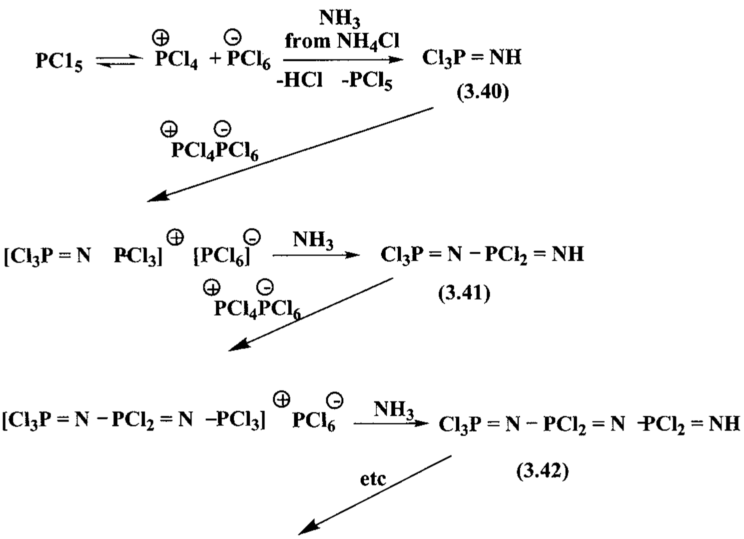
Conversely, if the polymer could be made by some other route (for example, by macromolecular substitution), it might be stable at moderate temperatures where the rate of depolymerization is very slow, but would depolymerize to the cyclic trimer or tetramer when heated to higher temperatures. In fact, this behavior is found for uncross-linked polymers such as $[NP(OPh)_2]_n$, that appear to be kinetically stabilized at moderate temperatures, but are sufficiently destabilized thermodynamically by the bulky aryloxy side groups that they depolymerize when heated above 150–200 °C.

3.3.5 Condensation Polymerizations That Yield Poly(dichlorophosphazene)

Ring-opening polymerization of $(NPCl_2)_3$ is not the only way to produce poly (dichlorophosphazene), although it is the method that gives the highest molecular weight polymers. Certain condensation polymerizations can also lead to this polymer, which is then used as a macromolecular intermediate for reactions with alkoxides, aryloxides, or amines. Three different condensation processes have been identified, and are discussed in the following paragraphs.

Condensation of PCl_5 with Ammonia

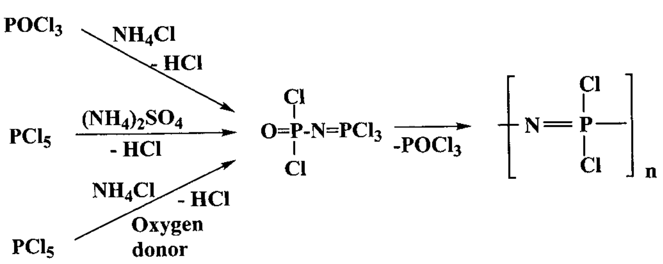
As discussed, condensation reactions form the basis of the synthesis of the cyclic trimer, $(NPCl_2)_3$. The reaction between phosphorus pentachloride and ammonia or ammonium chloride proceeds in a stepwise fashion, as shown in reaction sequence (18), by elimination of hydrogen chloride first to form a monomer (**3.40**), then a linear dimer (**3.41**), trimer (**3.42**), tetramer, and so on. Cyclization could occur to give cyclic chlorophosphazenes at any stage beyond the dimer, but in practice is less likely as the chains grow beyond a certain length. Several authors have extended this process to produce relatively low molecular weight poly(dichlorophosphazene).[36–39]



(18)

Condensation Reactions of $OCl_2PN{=}PCl_3$

De Jaeger and coworkers[40–43] have carried out extensive studies on the polymerization of the monomer, $OCl_2PN{=}PCl_3$, which is prepared from (a) PCl_5 and ammonium sulfate, (b) phosphoroyl chloride and ammonium chloride, or (c) PCl_3 and ammonium chloride under oxidative conditions. At 240–290 °C and at atmospheric pressure, this monomer eliminates phosphoroyl chloride, $POCl_3$, and yields poly(dichlorophosphazene). The overall processes are shown in reaction (19). The advantage of this method is its low cost. Disadvantages are the broad molecular weight distributions generated and the lower molecular weight polymers than those produced from $(NPCl_2)_3$. Nevertheless, this process has been used commercially.

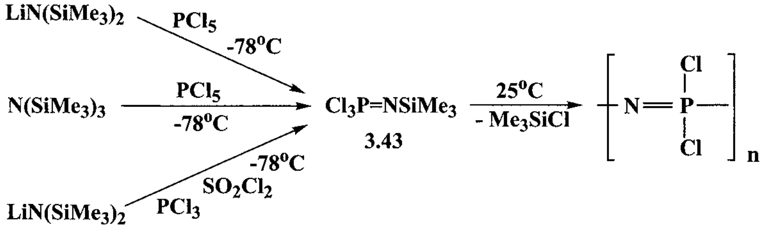


(19)

Living Cationic Polymerization of $Me_3SiN{=}Cl_3$

The newest condensation reaction to poly(dichlorophosphazene), developed by Allcock, Manners, and their coworkers,[44–47] uses an *N*-silylphosphoranimine, $Me_3SiN{=}Cl_3$ (**3.43**), as a monomer for bulk or solution phase polymerizations at room temperature in the presence of small amounts of Lewis acids as initiators. The process yields

polymers with very narrow molecular weight distributions, allows control of the molecular weight through changes to the ratio of monomer to initiator, and provides access to block and comb copolymers of polyphosphazenes with organic polymers and silicones (see later). In this sense, this approach overcomes many of the drawbacks of the other processes, but it is currently the most expensive route and has not yet been scaled up to the commercial level. The monomer is prepared by the three methods indicated in reaction (20), and the polymerization mechanism is believed to be the one shown in reactions (21) and (22). The living cationic chain ends produced in reaction (22) may be terminated by the addition of a phosphoranimine that bears a functional site. This is the basis of the formation of block, graft, and comb copolymers (see later).



(20)

Initiation

$$Cl_3P{=}NSiMe_3 \xrightarrow[-\ Me_3SiCl]{2\ PCl_5} Cl_3P{=}N\text{-}PCl_3^+\ PCl_6^- \qquad (21)$$

Chain Growth

$$Cl_3P{=}N\text{-}PCl_3^+\ PCl_6^- \xrightarrow[-\ Me_3SiCl]{Cl_3P=NSiMe_3} Cl_3P{=}N\left(PCl_2{=}N\right)_n PCl_3^+\ \ PCl_6^- \qquad (22)$$

"Living" polymer end units initiate more of the same monomer, or a different phosphoranimine monomer, or react with a functional chain terminator to give an end-functionalized polyphosphazene.

Halogen Replacement

$$Cl_3P{=}N\left(PCl_2{=}N\right)_n PCl_3^+\ \ PCl_6^- \xrightarrow[-\ NaCl]{NaOR} (RO)_3P{=}N\left(P(OR)_2{=}N\right)_n P(OR)_{3\ \text{or}\ 4}$$

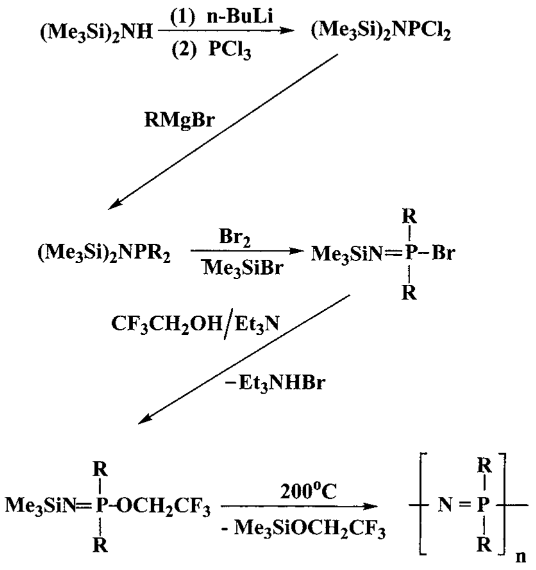
3.3.6 Condensation Polymerization of Organic Substituted Phosphoranimines

The living cationic polymerization described above can also be used for the direct production of poly(organophosphazenes). Thus, treatment of *N*-silylphosphoranimines such as $Me_3SiN{=}PCl_2R$ or $Me_3SiN{=}PClR_2$ in the presence of a Lewis acid initiator yields polymers of the type, $(NPClR)_n$ and $(NPR_2)_n$.[44,46,48–52] Polymers that bear one chlorine and one organic group per phosphorus can, of course, be converted to fully organo-substituted species by treatment with organic nucleophiles.

The first organophosphoranimine polymerization was reported in 1977 by Flindt, Rose, and Marsmann.[53,53a] They found that the trifluoroethoxy-substituted monomer,

$Me_3SiN{=}P(OCH_2CF_3)_3$, when heated at 200 °C, eliminated $Me_3SiOCH_2CF_3$ and yielded the polyphosphazene, $[NP(OCH_2CF_3)_2]_n$. This process was later refined by Matyjaszewski and coworkers who showed that higher molecular weight polymers could be produced from the same monomer with the use of anionic initiators such as Bu_4NF.[54–56]

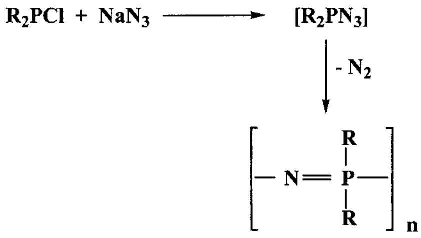
However, the principal contributors to the direct synthesis of poly(organophosphazenes) were Wisian-Neilson, Neilson, and their coworkers[57–60] who showed that a variety of trifluoroethoxy-substituted *N*-silylphosphoranimines can be converted to high polymers simply by heating in a closed system at 200 °C. The overall process is summarized in reaction sequence (23). Perhaps the most interesting examples of these transformations involve the synthesis of $(NPMe_2)_n$, $(NPEt_2)_n$, $(NPPr_2)_n$, and especially $(NPMePh)_n$. These are poly(organophosphazenes) that are difficult or impossible to prepare by macromolecular substitution reactions from $(NPCl_2)_n$ or $(NPF_2)_n$. The mixed-substituent polymer, $(NPMePh)_n$, has been used widely by these authors as a substrate for secondary substitutions via the lithiation of the methyl groups (see later). It is interesting that monomers, such as $Me_3SiN{=}PClR_2$, that eliminate a halogen under these conditions, yield small-molecule cyclic phosphazenes rather than high polymers.



(23)

3.3.7 The Azide Condensation Process

An alternative type of condensation synthesis involves the decomposition of organophosphorus azides. First reported by Haber and coworkers in the 1960s,[61] these syntheses follow the pathway shown in reaction (24), in which elimination of nitrogen takes place in solution with the direct formation of either a cyclic phosphazene or a polymer. Matyjaszewski and coworkers[62] have used this method to produce the nearly insoluble $(NPPh_2)_n$, which is difficult to prepare by other approaches, and $[NP(Ph)(p\text{-}MePh)]_n$ which is soluble in aromatic solvents. However, phosphorus azides are potential detonators, and they must be prepared and used in solution and not isolated in the solid state.



(24)

3.3.8 Secondary Macromolecular Substitutions

The primary polyphosphazene synthesis processes discussed above provide access to an enormous variety of different macromolecules. Yet further structural diversity can be achieved by carrying out modification reactions on the organophosphazene polymers produced in these primary rections. Secondary reactions are particularly important for the preparation of polymers with functional units in the side group structure, species that would be difficult or impossible to produce by the primary synthesis methods.

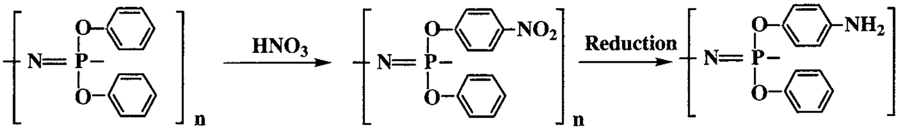
Many different secondary substitution reactions have been reported, and only a few representative examples will be mentioned here. Among those that are most widely used are organic transformations carried out on aryl rings that form part of the side-group structure. For example, poly(diphenoxyphosphazene) can be sulfonated with sulfur trioxide[63] or sulfuric acid,[64] or nitrated and then reduced to the amino-derivative.[65] Polymers with bromophenoxy side groups have been lithiated and the lithio-sites then converted to phosphine,[66] organosilicon,[67] organometallic,[68] or carboxylic acid moieties. As mentioned earlier, methyl side groups can be lithiated and then coupled to organosilicon or organometallic units.[60] Carboxylic acid ester side units can be deprotected by hydrolysis to give the free carboxylic acid units,[69] and a variety of protected amino and alcohol groups at the termini of both aromatic and aliphatic side groups have been subjected to deprotection reactions to give the amino or alcohol functional groups.[70] Typical secondary transformations are shown in reactions (25)–(28).

Secondary reactions of these types are widely used to produce polyphosphazenes that are required for biomedical applications or for polymer grafting reactions. They are also used to modify the surfaces of poly(organophosphazene), as discussed in the following section.

3.4 Surface Reactions of Polyphosphazenes

Some polymers have a specific set of bulk properties that make them ideal for a certain application, but cannot be used because the surface properties are inappropriate. For example, a material may have excellent elasticity but cannot be used in cardiovascular devices because the polymer surface triggers blood clotting. Alternatively, another polymer may have excellent surface biological compatibility but is too brittle for a cardiovascular application. An answer to this problem, like many others, is to select a polymer for its advantageous bulk properties and then carry out property modification reactions on the polymer surface without affecting the bulk material.

Poly(organophosphazenes) are particularly suited for surface reaction chemistry because a wide variety of primary organic side groups can be utilized, and these can be subjected to a variety or organic transformations. It is also useful that the polymer backbone in most



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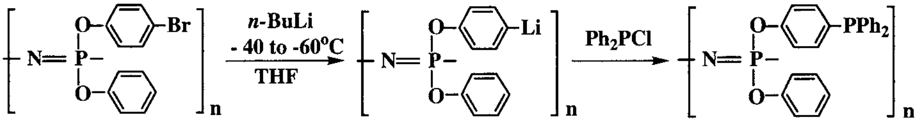

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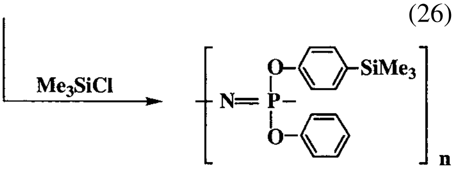

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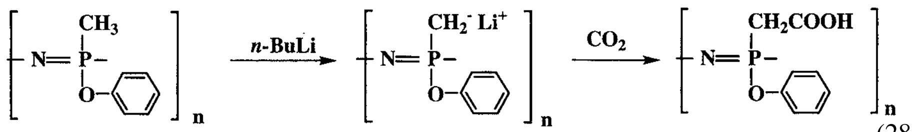


(28)

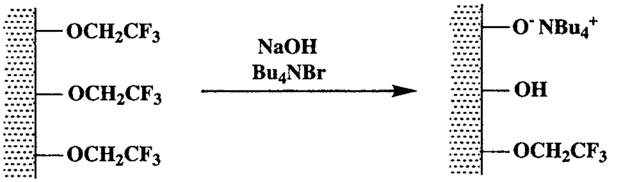
cases is protected from aggressive reagents by the side groups. Thus, a wide variety of surface reactions have been investigated in order to optimize different polymers for uses in medicine, surface coatings, adhesion, weather resistance, and for the immobilization of species such as enzymes or other biologically active molecules.[71–75] Reactions (29)–(33) summarize a few of the surface modifications that have been explored.

Note that many of these surface reactions involve the conversion of a hydrophophic polymer to one with a hydrophilic surface or vice versa. For example, the replacement of trifluoroethoxy groups at the interface by hydroxyl units changes a non-adhesive, highly hydrophobic surface to an adhesive hydrophilic one. Variations in the reaction conditions allow both the depth of transformation and the ratios of the initial to the new surface groups to be controlled. A possible complication that needs to be kept in mind for all of these surface transformations is that polymer molecular motions may bury the newly introduced functional units if the polymer comes into contact with certain media. For example, a hydrophilic surface on a hydrophobic polymer may become buried when that surface is exposed to dry air or a hydrophobic liquid. But this process can be reversed by exposure to a hydrophilic liquid.

3.5 Hybrid Systems through Block, Comb, or Ring-Linked Copolymers

3.5.1 Scope

Methods are now available for the hybridization of phosphazenes with other polymer systems in order to combine the special properties of the inorganic macromolecules with those of



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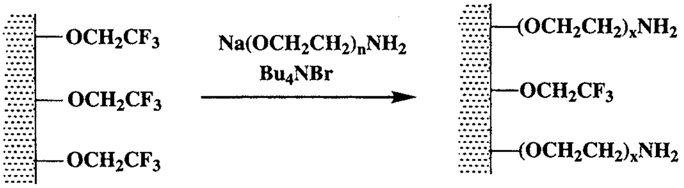

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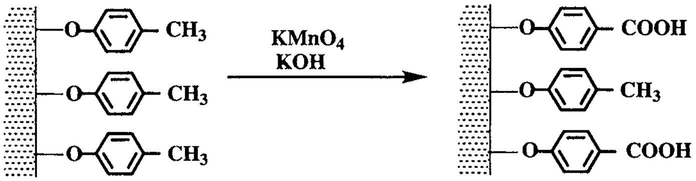

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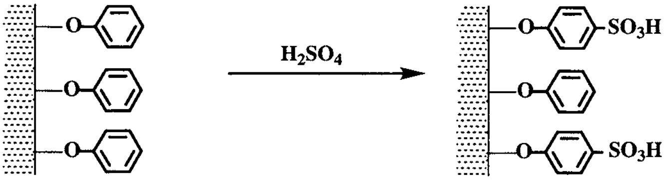

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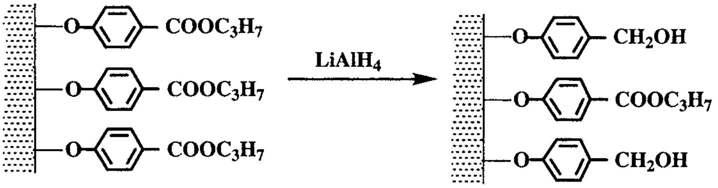
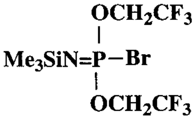


(33)

classical organic polymers or poly(organosiloxanes).[1] Hybrid systems have potential advantages, such as lowering the cost of a material or making use of special properties of the phosphazenes such as fire resistance, water repellency, ease of binding of biological agents, and so on. Hybridization can be accomplished in several different ways. First, block copolymers can be produced by use of the living cationic polymerization discussed earlier and by the conversion of living polymers to end-functionalized or telechelic macromolecules. Second, polyphosphazenes can be prepared with vinyl, allyl, or norbornenyl groups at the chain terminus, and these may be polymerized or copolymerized with unsaturated organic monomers to yield organic polymers with pendent polyphosphazene side chains (comb or graft copolymers). Third, small molecule phosphazene rings can be functionalized with vinyl, allyl, or norbornenyl side units, and polymerization of these yields organic polymers with cyclophosphazene side groups. Finally, phosphazene rings can be joined together through organic polymer or oligomer linkage units to form cyclolinear or cyclomatrix materials. These systems will be considered in turn.

3.5.2 Block Copolymers

The living cationic polymerization of *N*-silylphosphoranimines, discussed in Section 3.3.5 yields "living" macromolecules that react with phosphoranimine *terminators*. Alternatively, the same molecules that serve as terminators may also be used as *initiators* from which polyphosphazene chains may be grown. The terminators and initiators have the general formula, $Me_3SiN{=}PR_2R'$, in which R is an unreactive organic group such as trifluoroethoxy and R′ is a unit that bears some functionality. Examples are shown as **3.44–3.49**.[76–79] That functionality may be a vinyl, allyl, or norbornenyl group or some other unit that can be used to couple the phosphazene to the end of another macromolecule. Provided R′ is not a halogen atom, X, which would be eliminated as Me_3SiX, termination of the phosphazene chain occurs in preference to further polymerization. This is illustrated in reaction sequence (34).



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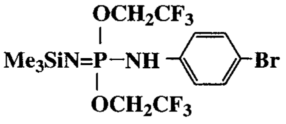

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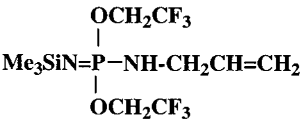

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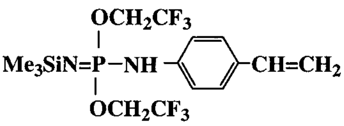

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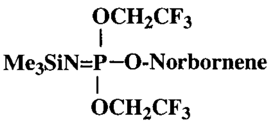

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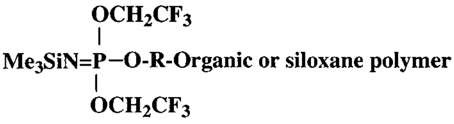
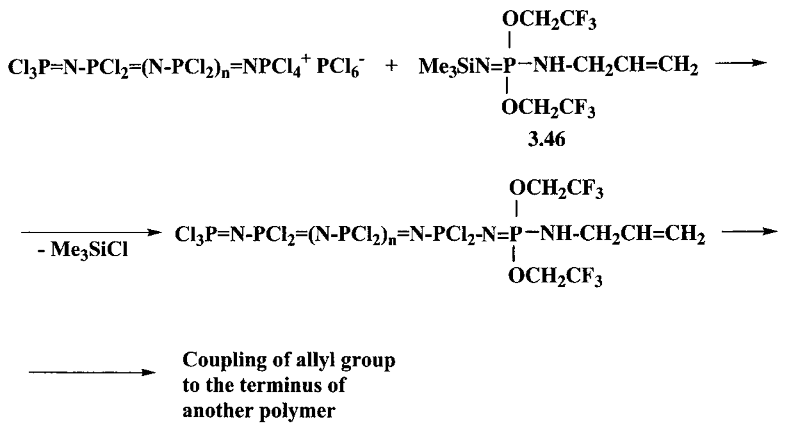


3.49

Note that, after the polymerization has been terminated by the terminator phosphoranimine, the chlorine side units along the polyphosphazene chain must be replaced by unreactive organic units before proceeding to the polymer end-linkage step. Note also that, depending on the initial ratio of PCl_5 to monomer, the unterminated polyphosphazene may have one living end, or be active at both ends. Thus, the termination process can provide a structure that is appropriate for linkage to another polymer through one or both termini to give diblock or triblock copolymers (**3.12–3.14**). Alternatively, one of the initiator molecules, such as **3.44**, can be coupled to the end of an organic polymer and then used to initiate growth of a poly(dichlorophosphazene) chain. Reaction sequence (35) illustrates this option. Block copolymers **3.50–3.53** are four examples synthesized by these techniques. In these structures Sw refers to a "switchover" group.



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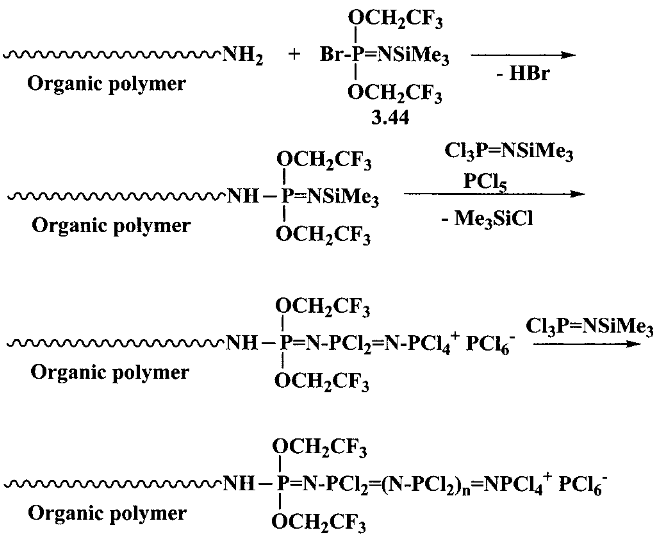
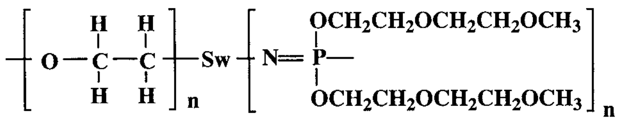


(35)

Block copolymers that contain segments with different characteristics, such as hydrophobic and hydrophilic blocks, can form phase-separated solid systems, or they can be employed to form micelles or vesicles in aqueous media. Considering that the lengths of each polymer block can be controlled, the opportunities for property variations are almost infinite through such systems.

3.5.3 Comb and Graft Copolymers

Comb or graft polymers (**3.15**) are accessible through the polymerization of vinyl, allyl, or norbornenyl units that are linked covalently to the end of polyphosphazene chains.[80] As mentioned earlier, this can be accomplished via the termination of a living polyphosphazene chain by a phosphoranimine that bears one of these units. The comb copolymer is then produced by free-radical or ring-opening metathesis polymerization (ROMP) of the functional groups. Alternatively, copolymerization with organic monomers can yield graft copolymers. Two examples are shown in reactions (36) and (37).



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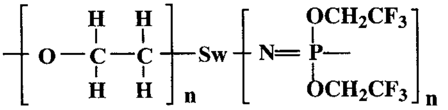

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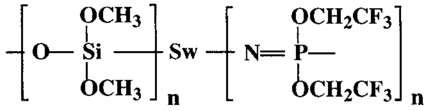

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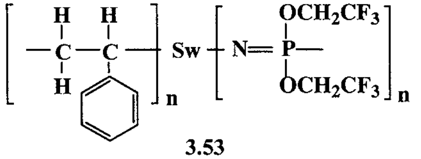


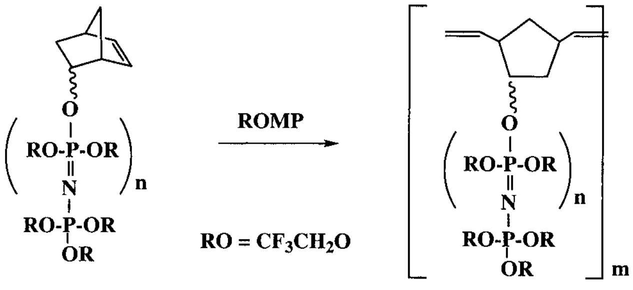
3.53

Organic polymers with polyphosphazene grafts or polyphosphazenes with organic polymer grafts can also be produced by the photolysis or radiolysis of mixtures of the two types of polymers.[81]

3.5.4 Organic Polymers with Phosphazene Rings as Side Units

The cyclic trimeric phosphazene ring is a stable unit with valuable technological properties, such as heat resistance and flame retardant behavior. Thus, organic polymers that contain small-molecule phosphazenes have a much lower flammability than their counterparts in which the phosphazene is absent. A fire-resistant Rayon (regenerated cellulose) has been manufactured that contains alkoxycyclophosphazenes physically trapped in the organic polymer fibers.[82] However, for many applications it is more useful to have phosphazene rings bound *covalently* to an organic polymer chain rather than simply trapped within this material. In this way a fire retardant small-molecule phosphazene cannot escape by diffusion over a long period of time.

Three methods have been developed to bring about this linkage. In the first, cyclophosphazene rings have been synthesized that bear one vinyl or allyl group per ring.[83–86] An example monomer is shown as **3.54** in reaction (38). Second, norbornenyl groups can be linked to phosphazene rings, as shown in **3.55**, and these can be polymerized or copolymerized with norbornene using ROMP initiators as shown in reaction (39).[87,88] Third, a method has recently been developed to link azido-phosphazene rings (**3.56**) to phosphonated polystyrene, as illustrated in reaction (40).[89]



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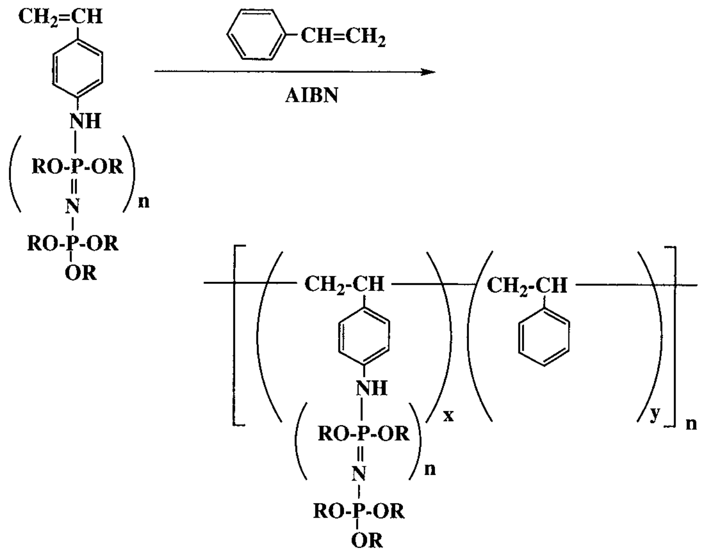
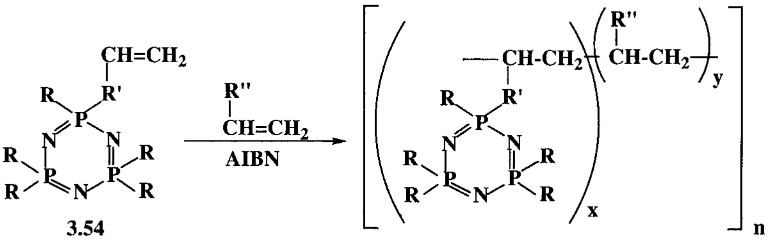


(37)

3.5.5 Cyclolinear Copolymers

Phosphazene rings can also be incorporated into organic polymers though cyclolinear (**3.18**) and cyclomatrix (**3.19**) polymers. Cyclolinear species are accessible via the reactions of cyclic trimeric or tetrameric phosphazenes that contain only two functional side groups, the other side groups being non-reactive units. Two methods are available to do this. First, a cyclic trimeric or tetrameric phosphazene ring that contains four or six inert organic side groups and two non-geminal chlorine atoms is first prepared by the reaction of $(NPCl_2)_3$ or $(NPCl_2)_4$ with a stoichiometric deficiency of an alkoxide, aryloxide or amine. This compound is then allowed to react with a difunctional organic chain, for example with a diol or diamine (reaction (41)). Numerous variations on this approach have been reported. Difficulties with this method include ensuring that only two chlorine atoms remain on the cyclophosphazene, and guaranteeing that the two monomers are present in an exact 1 : 1 ratio. Failure to do either of these things will bring about cross-linking (with three or more chlorine atoms) or low-molecular-weight oligomers (if one monomer is present in slight excess). Another problem with this approach is that long organic polymer chains with terminal alkoxide or amino groups



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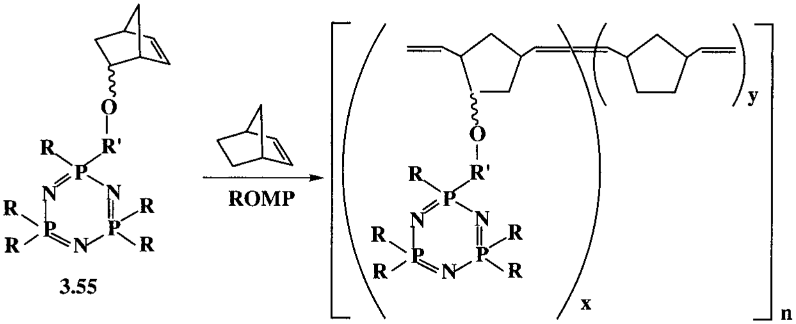

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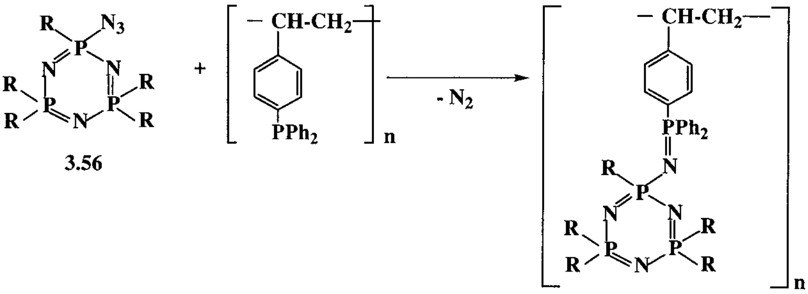

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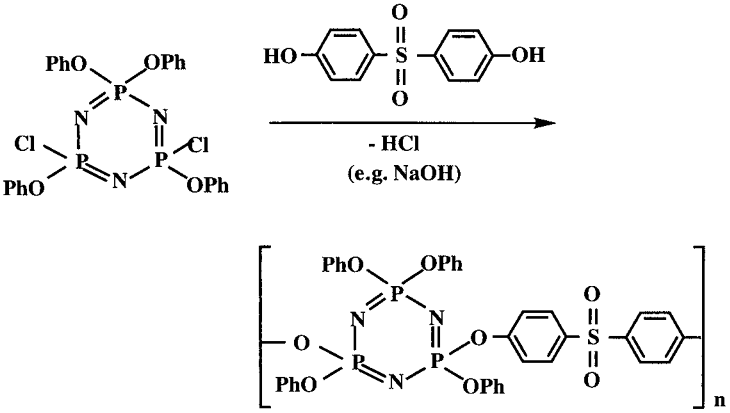
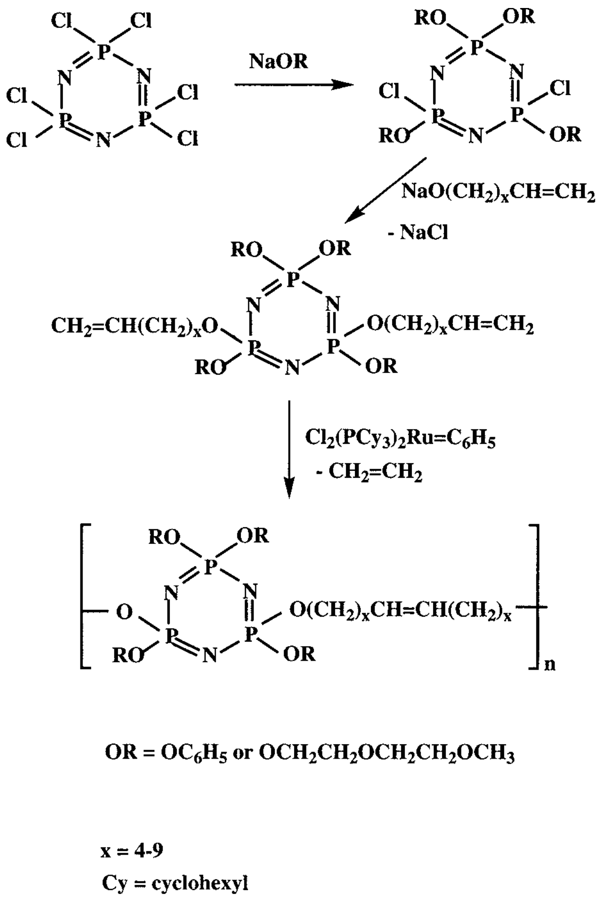


(41)

may require very long reaction times or forcing conditions to overcome the statistical improbability that all the reactive units will find each other in the reaction mixture.

An alternative, and more recent, approach is shown in reaction (42).[90,91] Here, a cyclophosphazene is synthesized with two non-geminal alkoxy chains that bear terminal olefinic groups. Treatment of these compounds with an organometallic ADMET catalyst causes loss of ethylene and formation of a cyclolinear polymer. The chain lengths achieved by this method are generally longer than those produced by the dehydrohalogenation technique.



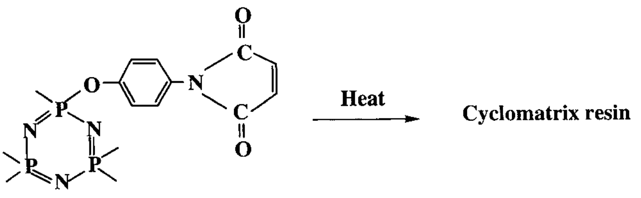
(42)

3.5.6 Cyclomatrix Copolymers

If a cyclophosphazene precursor molecule has more than two reactive sites (e.g. chlorine atoms), linkage reactions with diamines of dialkoxides will generate a three-dimensional structure rather than a linear chain. Such materials are known as cyclomatrix polymers (**3.18**). These species form a half-way stage between linear polymers and ceramics, and occupy a critical position in materials science. The term "ultrastructure" covers a broad range of materials of this type.

The difference between a linear or macrocyclic polymer and an ultrastructure is one of rigidity and thermal stability with both of these properties increasing with the density of cross-linking. Most ceramics such as silicates, silicon nitride, or silicon carbide are totally inorganic materials held together by a tightly knit three-dimensional array of covalent bonds. However, organic ultrastructures are also known. One example is the melamine-formaldehyde resin in which *s*-triazine rings are linked together by a three-dimensional framework of organic cross-links.

Many different cyclomatrix systems have been reported that are based on cyclotriphosphazene rather than an *s*-triazine rings.[92,93] In these materials a difunctional nucleophile, such as a diamine or an aromatic diol or disodium diol, is used to link together the cyclophosphazene rings.[117] Cyclophosphazenes with *p*-aminophenoxy side groups are readily converted into ultrastructures by reaction with maleic anhydride, as shown in reaction (43).[118] These materials are reported to have a very high thermal stability, a property needed for use as high temperature coatings.



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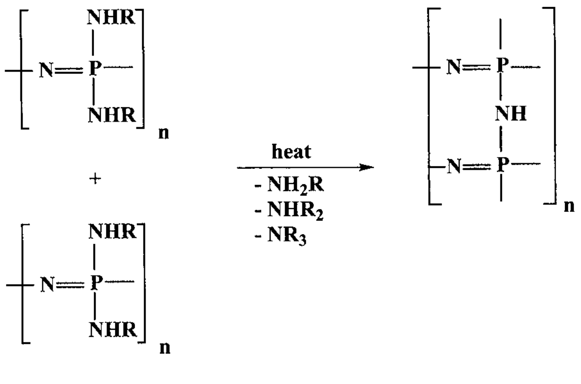


(44)

3.5.7 Inorganic Ceramics Derived from Phosphazenes

Ceramic-type materials that contain no organic linkage units can be prepared by the pyrolysis of cyclic or high polymeric aminophosphazenes. An example is shown in reaction (44). Under appropriate conditions, pyrolysis products that correspond to phosphorus-nitride are formed. Polyphosphazenes that contain both amino and borazine side groups yield phosphorus-nitrogen-boron ceramics following pyrolysis.[94,95] The conversion of a formable polymer into a ceramic has many potential advantages for the controlled synthesis and fabrication of advanced ceramics. This principle is discussed in more detail in Chapter 9.

3.6 Hybrid Systems through Composites

The formation of hybrid macromolecules through the linkage of organic polymers to polyphosphazenes is only one of several different approaches to produce hybrid systems. Another approach, which draws on materials science more than chemistry, involves the mixing of two polymers in the solid state—in this case a polyphosphazene with an organic polymer. Two situations can be envisaged. In the first, the two polymers are intimately mixed either mechanically or by combining solutions of the two followed by removal of the solvent by evaporation. These are called polymer blends or polymer alloys. In the second approach, the two polymers are combined, and then one or both are cross-linked to prevent the individual chains from segregating and causing phase separation. In practice, this second method is achieved by swelling a cross-linked version of the first polymer (i.e. the polyphosphazene) by the monomer of the second, followed by polymerization and possibly cross-linking of the second component. Such hybrid systems are called interpenetrating polymer networks or IPNs.[96]

Examples of known phosphazene polymer blends are those in which phosphazenes with methylamino, trifluoroethoxy, phenoxy, or oligo-ethyleneoxy side groups form blends with poly(vinyl chloride), polystyrene, poly(methyl methacrylate), or poly(ethylene oxide).[97–100] IPNs have been produced from $[NP(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$ (MEEP) and poly(methyl methacrylate).[101–103] In addition, a special type of IPN has been reported in which a water-soluble polyphosphazene such as MEEP forms an IPN with a silicate or titanate network generated by hydrolysis of tetraethoxysilane or tetraalkoxytitanane.[104] These materials are polyphosphazene/ceramic composites, which have been described as suitable materials for the preparation of antistatic layers in the manufacture of photographic film.

3.7 Organometallic Polyphosphazenes

3.7.1 General Observations

Polymers form one segment of the four main areas of materials science (Figure 3.6). One of the main motivations for exploratory research work with inorganic polymers is to develop the area that lies between organic polymers, metals, and ceramics. The development of polyphosphazene synthesis research has taken place with this in mind. For example, the use of a wide variety of organic side groups attached to a phosphazene backbone has permitted materials to be developed with "organic-like" properties. In this section, we consider polyphosphazenes that have metal atoms in the side group, and which occupy the interface between polymers and metals.

Three approaches to the synthesis of metallophosphazenes have been explored, and these are summarized by the three repeating units shown as **3.57–3.61**.

3.7.2 Coordination Compounds

Platinum Coordination to the Backbone

Conceptually, the simplest approach to metallophosphazenes is the one shown in **3.57**, in which the lone-pair electrons of the skeletal nitrogen atoms are used to coordinate metal atoms to the skeleton. Only one example will be given of this arrangement,

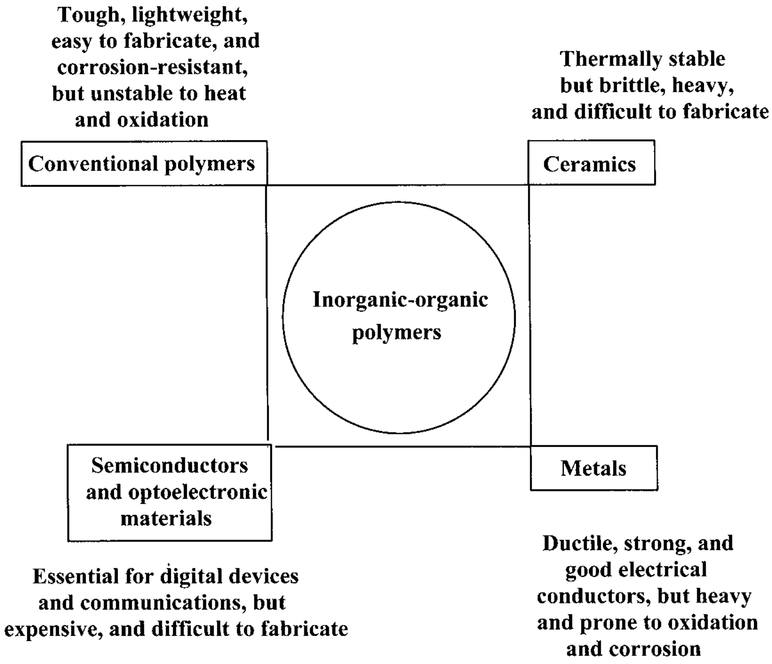
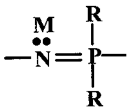


Figure 3.6 Illustration of the four main areas of materials science and the way in which they come together through the field of inorganic-organic polymers. Advanced materials are now being discovered where these area overlap.



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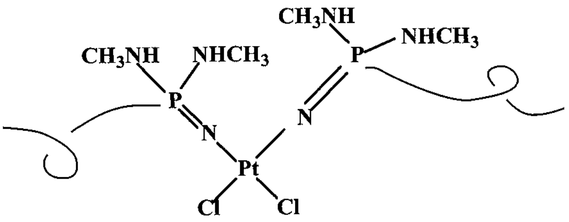

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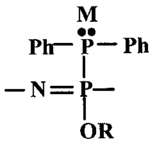

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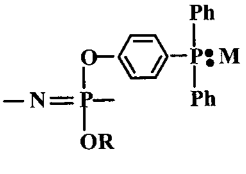

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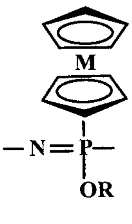


3.61

although the principle could be applied widely. The example is the binding of $PtCl_2$ units to give an experimental polymeric antitumor agent. Specifically, the water-soluble, water-stable polyphosphazene shown in **3.32** reacts with aqueous $PtCl_2$/18 crown-6 ether to give polymer **3.58**.[90] Only a low loading of $PtCl_2$ can be tolerated (approximately one platinum atom per 17 repeating units) because larger amounts tend to cross-link the chains and render the system insoluble. However, the evidence from model compound studies[105] suggests that it is the *skeletal* rather than the side-group nitrogen atoms that form the coordination sites. This is presumably a consequence of the strong electron supply from the amino side groups that enhances the coordination character of the skeletal nitrogen atoms.

Metals Linked to the Polymer through Organic or Inorganic Spacer Groups

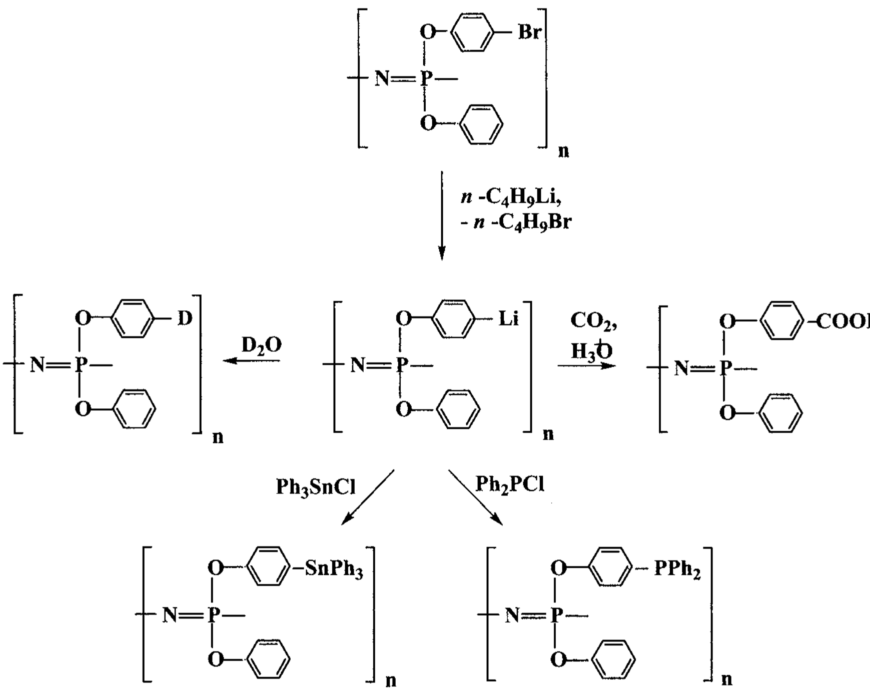
A number of organic side groups have been utilized as "spacer" units to link transition metals to a polyphosphazene chain. Some of the spacer units are depicted in structures **3.59–3.61**.

Species of type **3.59**, in which a phosphine donor unit is linked to a skeletal phosphorus atom by a P-P bond are the least stable species, and the most difficult to prepare.[106] Specifically, they are synthesized by the reaction of P-Cl bonds in the polymer with lithium triethylborohydride, $LiBEt_3H$, which generates a P^- site in place of the P-Cl bond. Treatment of the polymer with Ph_2PCl then yields side groups of the type shown in **3.59**. Reaction with $Ru_3(CO)_{12}$ results in the linkage of $Ru_3(CO)_{11}$ units (M) to the side groups.

The spacer units in **3.60** are assembled from polyphosphazenes that bear *p*-bromophenoxy side groups via a lithiation reaction, and treatment with a diorganochlorophosphine to give **3.62**. The chemistry is summarized in reaction sequence (45).[107] Polymer **3.62** coordinates to a variety of metallo species,[108] including osmium cluster compounds and cobalt carbonyl hydroformylation catalysts. When used as a polymeric hydroformylation catalyst, this latter species proved how stable the polyphosphazene backbone is under the drastic conditions often needed for these types of reactions. The weakest bonds in the molecule proved to be those between the phosphine phosphorus atoms and the aromatic spacer groups.

Metals ions such as silver or mercury have been coordinated to thioether side chains linked to a polyphosphazene skeleton.[109]

The linkage of ferrocenyl and ruthenocenyl side units to a polyphosphazene has been accomplished via the chemistry shown in reactions (46) and (47).[110] Two situations exist: one in which the metallocene is linked to the polymer through one carbon-phosphorus bond (**3.63**), and the other where the metallocene forms a bridge between two adjacent phosphorus atoms (**3.64**). Polymers **3.63** and **3.64** are of interest for two reasons. First, they can be doped oxidatively with iodine to give polymers that are weak semiconductors. Second, when deposited on an electrode surface the polymers serve as electrode "mediator" coatings that assist electron transfer between a reagent in solution and the electrode.[111] Free ferrocene, for example, would not remain in the vicinity of the electrode surface. An electro-inactive polymer is needed to immobilize the metallocene in the region of the electrode surface. Copolymerization of phosphazene trimers that bear ferrocenyl and ruthenocenyl side groups is possible, and the resultant polymers bear sites with different oxidation potentials. Such polymers are of particular interest in electrode mediator catalysis.



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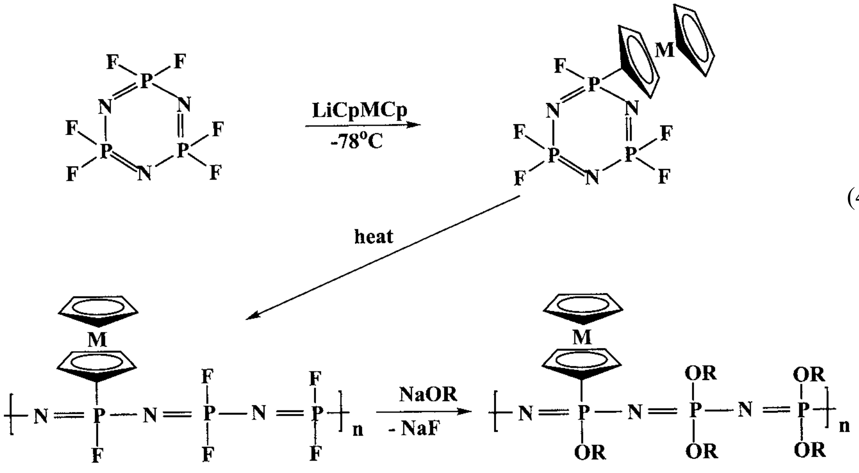
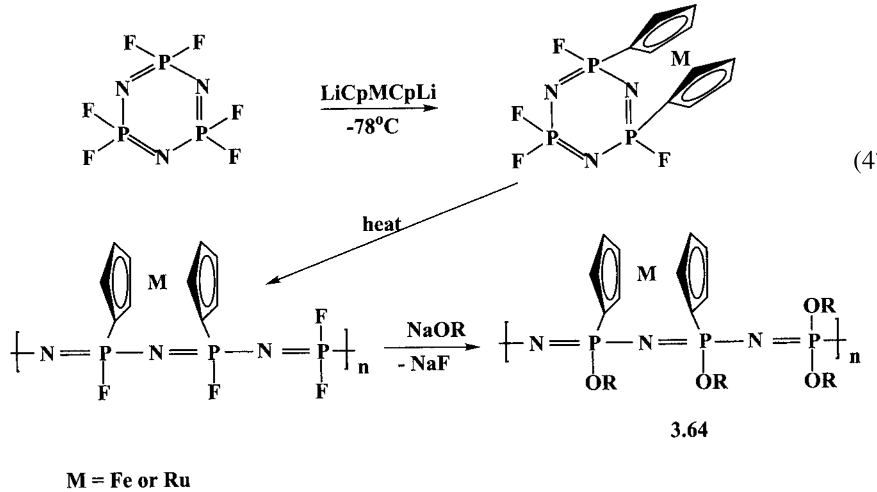
3.62



(46)

3.63

A series of cobalt carbonyl complexes of polyphosphazenes have been prepared via arene coordination sites. Examples are shown as **3.65** and **3.66**.[112] These are synthesized via the reactions of $(NPCl_2)_n$ with the sodium salt of the appropriate metal-arene terminated alcohol. Mixed-substituent polymers with trifluoroethoxy or phenoxy cosubstituents have also been prepared.



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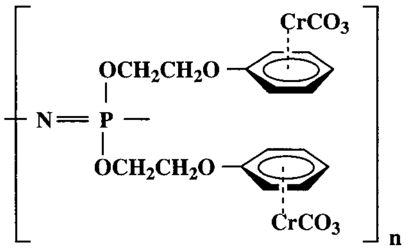

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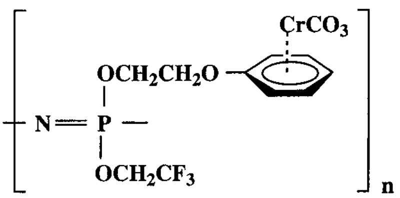
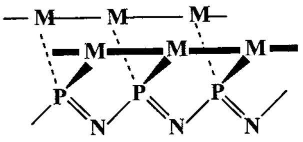


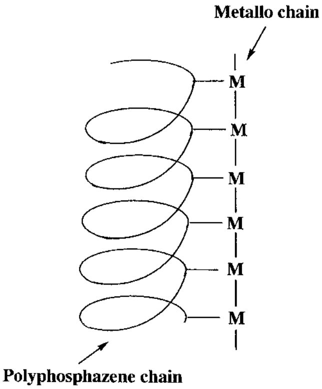
3.66

3.7.3 Polyphosphazenes with Metal-Phosphorus Bonds

Polymers that consist of metal atoms joined together in a linear array are quite rare. This is because such systems prefer to collapse to three-dimensional clusters—literally very small chunks of metal stabilized on the surface by ligands. However, many of the intriguing electrical properties proposed for linear metallo polymers might be realized if a non-metallo polymer, such as a polyphosphazene, were used as a template and scaffold to stabilize a string of metal atoms and prevent cluster formation (structures **3.67** and **3.68**). This has been accomplished only in a very preliminary and tentative way,



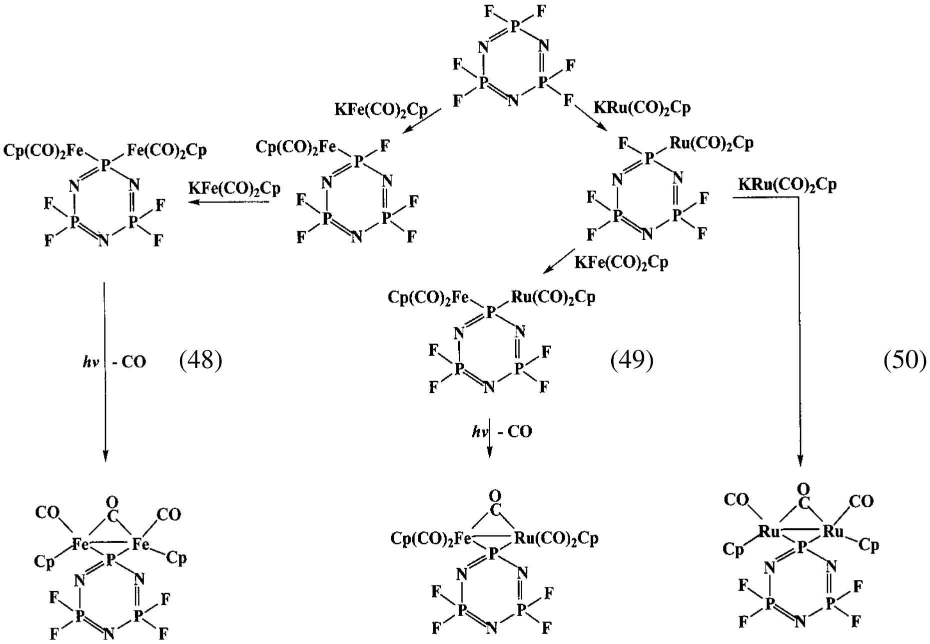
3.67

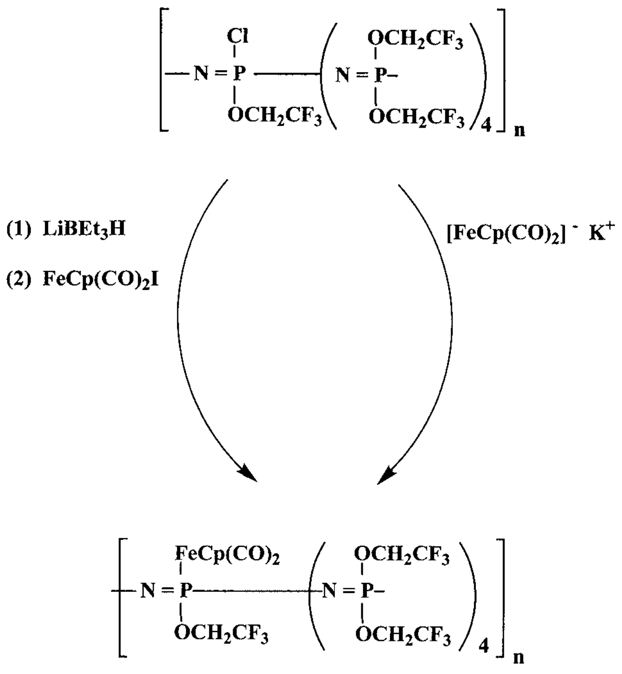


3.68

and mainly with small-molecule model systems rather than with high polymers.[113–115] Nevertheless, the results are instructive and perhaps predictive.

Consider the set of model compound reactions shown in reactions (48), (49), and (50). These are prototypes reactions which, if applied at the high polymer level, might yield polymers of the type depicted (idealistically) in **3.67** or **3.68**. Synthesis of species corresponding exactly to these structures has not been accomplished, but polymers that bear metal atoms linked to phosphorus every five or so repeating units have been prepared by the chemistry shown in reactions (51) and (52).[116] The aim of this type of work is to optimize the synthetic procedures to increase the loading of metal atoms to the point where metallic-like properties become evident.





(51) (52)

C_p = Cyclopentadienyl, C_5H_5

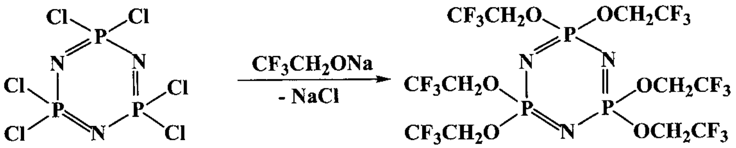
3.8 Small-Molecule Models

Most chemists begin their training by learning about small molecules rather than polymers. The reasons for this are both traditional and practical. Small molecules are often easier to synthesize, purify, and characterize than are polymers. Moreover, in phosphazene chemistry it is easier to study small-molecule reactions, reaction mechanisms, and molecular structures than it is to obtain comparable information at the high-polymer level.

For these reasons, small molecules have played a crucial role in the development of phosphazene high-polymer chemistry.[117] In particular, the substitution reactions, reaction mechanisms, NMR spectroscopy, and X-ray diffraction analysis of small-molecule cyclic phosphazenes, such as **3.2** or **3.3** have provided information that could not be obtained directly from the high polymers.

For example, one of the first clean reactions carried out between $(NPCl_2)_3$ and an alkoxide ion was the one shown in equation (53), that is the reaction of $(NPCl_2)_3$ with sodium trifluoroethoxide.[15,16,118] It was the isolation and study of this exceedingly stable derivative (**3.69**) that pointed the way to the use of the same nucleophile for the replacement of the chlorine atoms in $(NPCl_2)_n$ by fluoroalkoxy groups.[12,14]

The model compound approach is also useful for studying reaction mechanisms. For example, as chlorine atoms in $(NPCl_2)_3$ are replaced by OCH_2CF_3 groups, what is the *pattern* of halogen replacement? Does the second fluoroalkoxy group enter the molecule at the same phosphorus atom as the first, or at an unsubstituted phosphorus atom



3.69

(53)

(at the so-called non-geminal site)? Does this pattern persist when the same reaction is carried out on the high polymer? If not, what influence does a small-molecule ring or a linear chain have on the mechanism? Many of these questions have not yet been answered for most phosphazene polymer reactions, but they are critically important. Small-molecule reaction mechanism studies provide one of the few ways to answer these questions.[46]

It is exceedingly difficult to determine the molecular structure of a synthetic macromolecule. X-ray diffraction—the ultimate structural tool for small-molecule studies—yields only limited information for most synthetic high polymers, and crucial data about bond lengths and bond angles are difficult to obtain.[47] However, that same information can be obtained relatively easily from single crystal X-ray diffraction studies of cyclic trimers, tetramers, and short-chain linear phosphazene oligomers. The information obtained may then be used to help solve the structures of the high polymeric counterparts.

Of course, cyclic trimers and tetramers are not always good reaction or structural models for high polymers. The constraints of the ring may alter reactivities, bond angles, and bond lengths. But the model data provide a good starting point. And, generally, it is found that, if a certain reaction cannot be carried out with a phosphazene cyclic trimer or tetramer, it will not work for the high polymer.

3.9 Molecular Structure of Linear Polyphosphazenes

3.9.1 General Comments

Molecular structure determination for high polymers is a more complicated matter than is the corresponding process for small molecules. For one thing, different polymer molecules within the same sample usually have different chain lengths. In addition, if more than one type of side group is attached to the same polymer chain, the organization of those groups may differ from one point along the chain to another. For example, some regions of the chain may bear only one type of side group (a block structure), while another region may contain both groups organized in a radom or an alternating sequence. If the two are disposed in a regular, repetitive fashion, the arrangement may be isotactic, syndiotactic, or heterotactic.[119]

It should also be noted that, although most of the polymers discussed in this chapter are assumed to be linear open-chain structures, the possibility also exists that giant macrocyclic species or chain-linked macromolecules may also exist.[1] Such species would be very difficult to distinguish from linear high polymers. Linear polymers have end groups that, in theory, might be detectable by NMR techniques, but in practice the chains are

so long and the end groups so dilute that they usually cannot be detected. Thus, it is exceedingly difficult to distinguish between long chain polymers and large macrocycles or chain-linked structures. However, for the purposes of this discussion, it will be assumed that most polyphosphazenes are long-chain linear molecules.

Once the primary framework structure of the polymer has been determined, the question of chain conformation remains to be solved. Small molecules have access to only a limited range of molecular conformations, but polymer molecules, with their thousands of skeletal bonds and side group units, can adopt millions of different conformations—ranging from a totally random coil to extended chain or regular helical arrangements. Three physical tools have proved to be particularly useful for the structure determination of synthetic polymers—nuclear magnetic resonance (including magic angle spinning NMR), Fourier transform infrared spectroscopy, and fiber-type X-ray diffraction. Polyphosphazenes can be studied by all three methods, although the presence of several NMR-active nuclei (^{31}P, ^{13}C, ^{1}H, and often ^{19}F and ^{28}Si) makes nuclear magnetic resonance a particularly valuable technique. X-ray diffraction is a useful method for conformational studies.

In the following sections, four different aspects of polyphosphazene structure will be reviewed briefly: side-group disposition; chain conformation; skeletal bonding; and skeletal flexibility.

3.9.2 Side-Group Disposition

The properties of a polymer depend not only on the nature of the skeleton and the types of side groups attached to it, but also on the way in which different side groups are sequenced along the same chain. For example, isotactic or syndiotactic sequencing may favor efficient intermolecular chain packing and microcrystallite fromation. On the other hand, a random distribution of two or more different side groups will discourage crystallization, and may perhaps favor the appearance of elastomeric character.

Because most poly(organophosphazenes) are synthesized by a macromolecular substitution route, the disposition of side groups usually depends on the steric and electron-directing characteristics of the incoming groups and on the side groups already present. Thus, the order in which two or more different side groups are introduced will also affect the outcome.

The first step in the structural investigation of a polyphosphazene is to determine the side-group *ratios* by microanalysis and by NMR spectroscopy. The second step is to attempt to deduce the sequencing and configuration by a detailed analysis of the NMR spectra.

The ^{31}P NMR spectra shown in Figures 3.7 and 3.8 illustrate how the arrangement of side groups can be determined at the simplest level.

3.9.3 Macromolecular Conformations

The chain conformation of a macromolecule is determined by the torsional angles assumed by the backbone bonds. By convention, the angles 0°, 0° are used to define a *trans-trans*-planar conformation as shown in Figure 3.9a. Torsion (rotation) of bonds 2 and 4 in Figure 3.9a by 180° generates the *cis-trans*-planar conformation (Figure 3.9b).

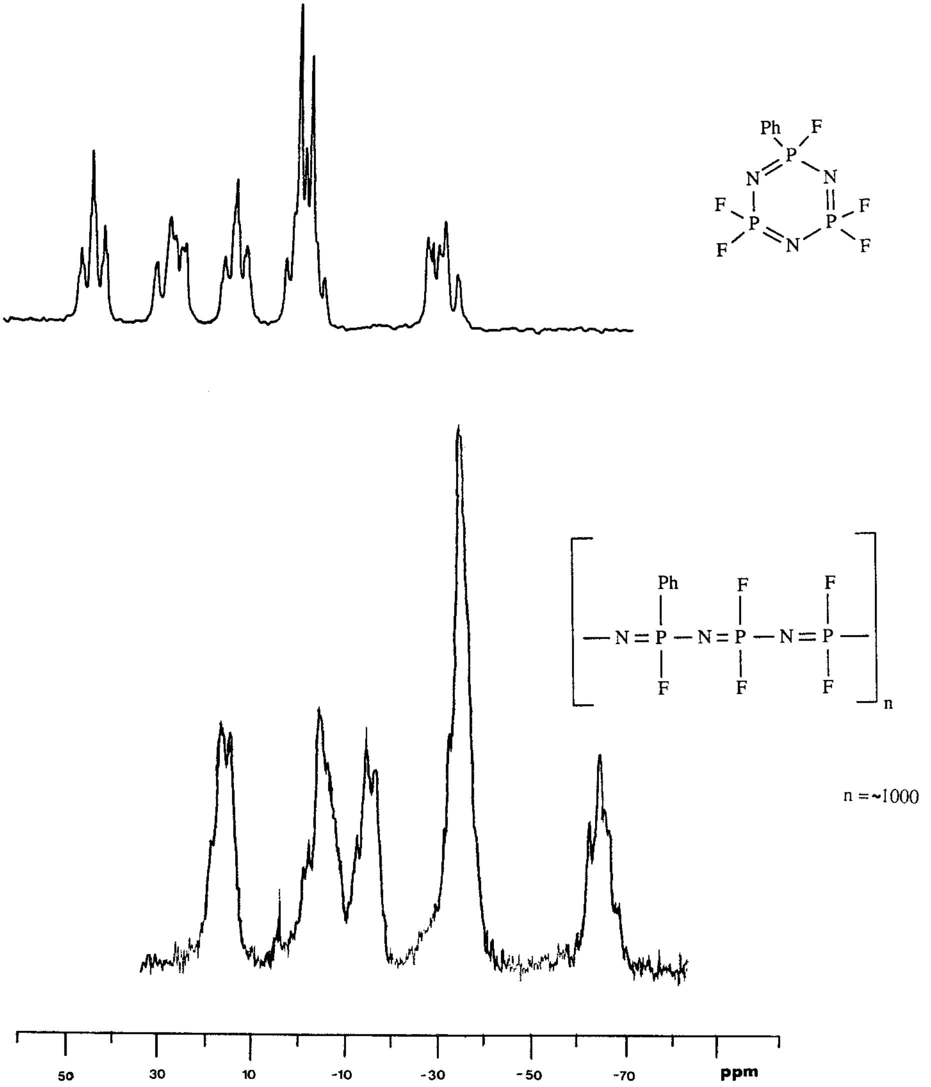


Figure 3.7 ^{31}P NMR spectra of cyclic trimeric and high polymeric phenyl-fluoro phosphazenes. Note (1) the shift in the whole spectrum that occurs in moving from a cyclic small-molecule phosphazene to a related high polymer, and (2) the chemical shift and splitting pattern that results from phosphorus coupling to the two fluorine atoms or to one fluorine. Spectra provided by W. D. Coggio.

Other torsional angle values can give rise to a broad range of spiral helices or even (if the torsional angles are not sequenced in some regular way) to a random coil.

In most polymers the torsional angles assumed by the molecule depend on two factors: (1) repulsions or attractions between nearby side groups on the same chain; and (2) the forces associated with the packing of many chains into a microcrystalline domain.

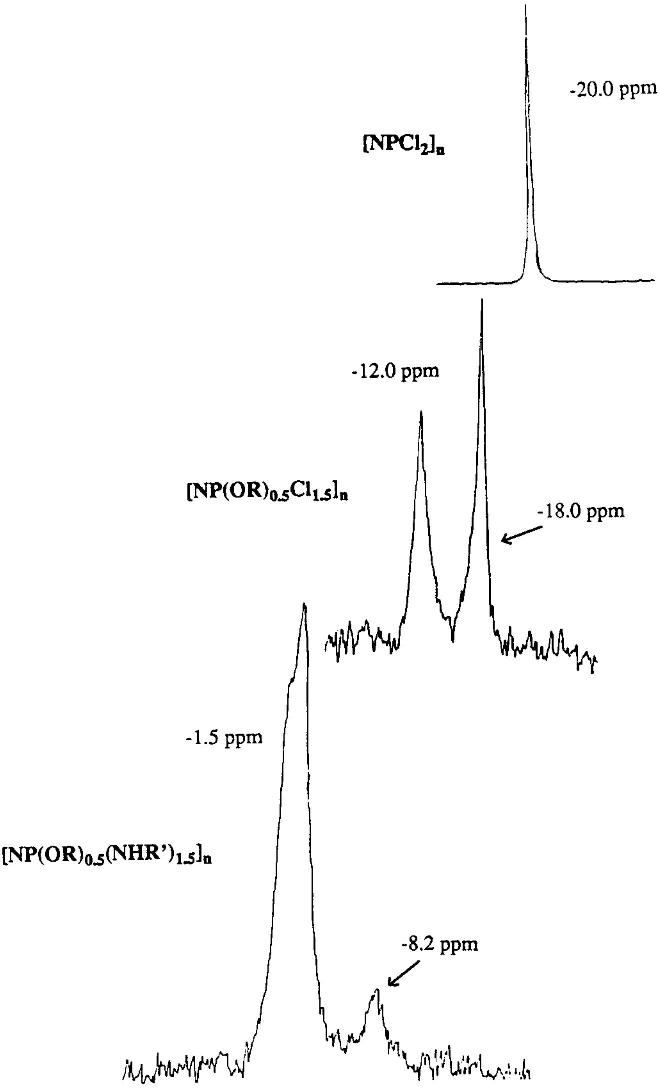


Figure 3.8 ^{31}P NMR spectral changes that occur when 25% of the chlorine atoms in $(NPCl_2)_n$ are replaced first by CF_3CH_2O- groups and the remainder by RNH- groups. The signal near 8.2 ppm in the spectrum of $[NP(OCH_2CF_3)_{0.5}(NHR)_{1.5}]_n$ results from blocks of $NP(OCH_2CF_3)_2$ units. Spectra provided by W. D. Coggio.

If organic-type double bonds are present in the chain, an additional influence will be exerted by the *cis-trans* barrier imposed by the p_π-p_π double bond.

For most polymers it is exceedingly difficult to predict the outcome of a balancing of all these influences. Hence, it is difficult to predict chain conformations. However, for polyphosphazenes, the situation is simpler than for most classes of macromolecules.

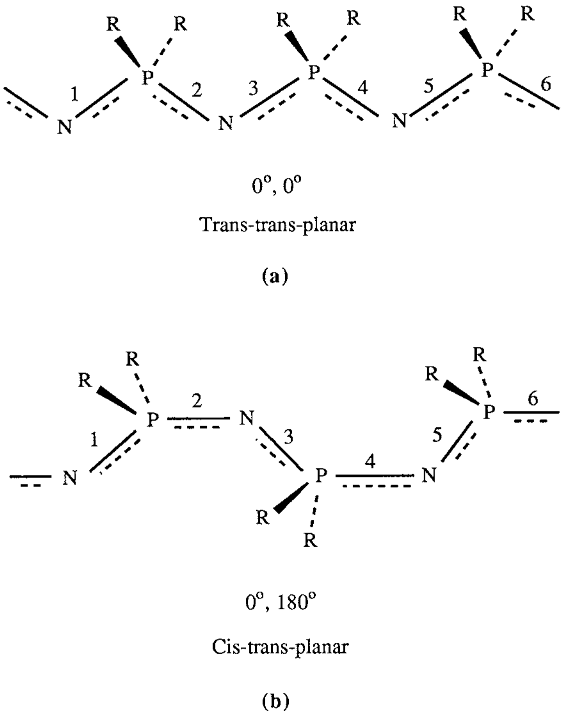


Figure 3.9 (a) *Trans-trans*-planar conformation of a polyphosphazene. (b) *Cis-trans*-planar conformation, the form detected for most of the phosphazene polymers studied to date.

First, in polyphosphazenes the side groups are attached to *every other* skeletal atom, rather than to every skeletal atom in the chain. This contrasts with the situation in most organic polymers. Second, although the structure of these polymers is written as a sequence of alternating single and double bonds, in fact the bonding is not of the classical organic p_π-p_π type, and it does not impose a skeletal torsional barrier (see later). It is as if all the backbone bonds behave like single bonds, at least so far as their torsional characteristics are concerned. Thus, the conformation assumed by a polyphosphazene can be understood mainly in terms of the repulsions or attractions between side groups attached to nearby phosphorus atoms. It can be seen from Figure 3.9 that the *cis-trans*-planar conformation allows the side groups to move as far away from each other as possible. Hence, this conformation should minimize the internal repulsions and generate the lowest energy. Molecular mechanics calculations tend to confirm this supposition.[120–123]

Of course, calculations of this type are interesting but not conclusive proof of the conformational preferences of a polymer. For one thing, they neglect the forces *between* neighboring polymer molecules. Experimental proof can be obtained by X-ray fiber diffraction experiments. A beam of X-rays passed through a stretched ("oriented") fiber of a microcrystalline polymer will yield a diffraction pattern. A diffraction pattern obtained for poly(dichlorophosphazene)[123] is shown in Figure 3.10. The separation of

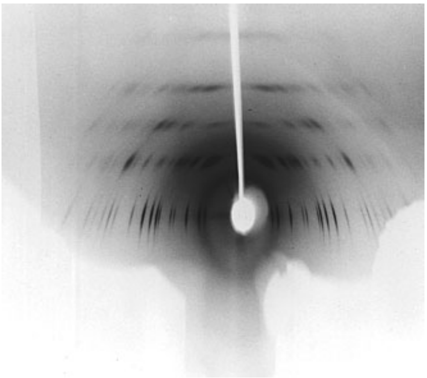


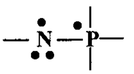
Figure 3.10 X-ray diffraction pattern obtained from a fiber of poly(dichlorophosphazene). The pattern of diffraction arcs is consistent with a near *cis-trans*-planar conformation of the polymer chains.

the horizontal layer lines in such a photograph gives an indication of the conformational repeating distance along the polymer chain. For virtually all polyphosphazenes studied so far (including those with F, Cl, CH_3, C_3H_7, OCH_2CF_3, OC_6H_5, and OC_6H_4Cl-*p* side groups), the repeating distance is close to 4.9 Å, which is the value expected if the chains assume a near *cis-trans*-planar conformation.[124–129] Moreover, the presence of a meridional reflection on the $l = 2$ layer line is an indication that there are two monomer units per turn of the "helix." This too is consistent with a near-*cis-trans*-planar arrangement of the chain.

The conformation of complex side groups that consist of more than one atom is more difficult to assess from X-ray fiber diagrams, and much work remains to be done to obtain detailed structural data for such polyphosphazenes.

3.9.4 Bonding in Polyphosphazenes

As mentioned earlier, the skeletal bonds in phosphazenes are unlike their counterparts in classical organic polymers. To understand the differences it is necessary to consider the disposition of the valence electrons in a short segment of the chain. Each phosphorus atom provides five valence electrons per repeating unit, and each nitrogen contributes an additional five. If two of the electrons from nitrogen are confined to a lone-pair orbital, and electron pairs are assigned to the sigma bond framework, two electrons are left unaccounted for—one from phosphorus and one from nitrogen (**3.70**). These electrons do not remain unpaired. It is believed that the electron on nitrogen is accommodated in a $2p_z$ orbital, and the one from phosphorus in a 3d orbital to generate an arrangement of the type shown in **3.71**.[130] Thus, although the pi-bonds are delocalized over "islands" of three skeletal atoms, they are not broadly delocalized over the whole chain because of the orbital mismatch and nodes that occur at every phosphorus. Moreover, because each phosphorus can use as many as five 3d-orbitals, torsion of a P-N bond can bring the nitrogen p-orbital into an overlapping position with a d-orbital at virtually any torsion angle. Hence, the inherent torsional barrier is much smaller than in a p_π-p_π double bond of the type found in organic molecules. Calculations suggest that the inherent torsional barrier in the backbone bonds may be as low as 0.1 kcal per bond.



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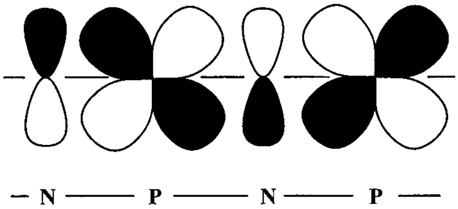


3.71

A number of investigators have reported *ab initio* calculations on polyphosphazenes, and various roles played by the phosphorus p- and d-orbitals have been proposed.[131–133] An "island" d_π-p_π bond structure may explain why most polyphosphazenes are colorless rather than colored materials, and are insulators rather than electronic conductors. Exceptions do exist, but the exceptions are for polymers that have chromophores in the side groups or which bear electroactive side units.

3.9.5 Skeletal Flexibility

A close connection exists between the presence of a flexible polymer skeleton and the flexibility of the bulk material. Macromolecular flexibility is often defined in terms of the glass-transition temperature, T_g. Below this temperature, the polymer is a glass, and the backbone bonds have insufficient thermal energy to undergo significant torsional motions. As the temperature is raised above the T_g, an onset of torsional motion occurs, such that individual molecules can now twist and yield to stress and strain. In this state the polymer is a quasi-liquid (an elastomer) unless the bulk material is stiffened by microcrystallite formation. Thus, a polymer with a high T_g is believed to have a backbone that offers more resistance to bond torsion than a polymer with a low T_g.

Polyphosphazenes are highly unusual macromolecules because specific polymers have some of the lowest T_gs known in polymer chemistry.[1] For example, $(NPCl_2)_n$ has a T_g of –66 °C,[15,16] $(NPF_2)_n$ has a value of –96 °C,[134] $[NP(OCH_3)_2]_n$ of –74 °C,[135] $[NP(OC_2H_5)_2]_n$ of –84 °C,[135] $[NP(OC_3H_7)_2]_n$ of –100 °C,[135] and $[NP(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$ of –84 °C.[136] Note that the low T_g values quoted are for polyphosphazenes that bear very small side groups (F, Cl, or OCH_3) or side groups that are themselves very flexible ($OCH_2CH_2OCH_2CH_2OCH_3$).

However, if the side groups are large and inflexible, they generate steric interference with each other as the skeletal bonds attempt to undergo twisting motions. Thus, as a general rule, large, rigid side groups impose their own restrictions on the flexibility of the macromolecule, even though the backbone bonds have a very low barrier to torsion. For example, if the side groups are OPh the T_g is –8 °C.[15,16] If the side units are -$OC_6H_4C_6H_5$-*p* the T_g is +93 °C. With adamantylamino side groups and trifluoroethoxy cosubstituents the T_g rises to 180 °C.[137]

It will now be clear why the polyphosphazene system is one of the most versatile polymer systems known. By the choice of appropriate side groups, polymers can be tailored to be low temperature elastomers, flexible, microcrystalline film and fiber forming materials, or high melting glasses. The choice of side group also affects properties such as solubility, refractive index, chemical stability, hydrophobicity or hydrophilicity, electrical conductivity, non-linear optical activity, and biological behavior. These effects are illustrated in the following sections.

3.10 Structure–Property Relationships

Enough is now known about the effect of different side groups attached to a polyphosphazene chain to allow some general structure–property relationships to be understood. To a limited extent, these relationships allow the prediction of the properties of polymers not yet synthesized. Some general relationships will be described in the following sections, but specific properties associated with certain side groups are summarized in Table 3.1.

3.10.1 Influence of Molecular Architecture

The molecular architecture of a polyphosphazene has a profound influence on properties. For example, linear and tri-star trifluoroethoxy-substituted polymers with the same molecular weight (1.2×10^4 or higher) have strikingly different properties.[138] The linear polymers are white, fibrous materials that readily form films and fibers, whereas the tri-arm star polymers are viscous gums. One is crystalline and the other is amorphous. Cyclolinear polymers are usually soluble and flexible. Cyclomatrix polymers are insoluble and rigid. Linear polymers can be crystalline, but graft or comb polymers are usually amorphous.

3.10.2 Crystalline versus Amorphous Polymers

As mentioned in Chapter 1 and earlier in this chapter, the presence of microcrystalline domains in an amorphous (random coil) polymer matrix has the effect of stiffening the material, generating opalescence rather than transparency, and raising the temperature at which the material can be used before it undergoes liquid-like flow.

Crystallization is a consequence of molecular symmetry. A macromolecule with a precise, regular sequence of side groups arrayed along the chain will be more prone to pack tightly with neighboring molecules than will a polymer that has an irregular disposition of side groups.

The conditions for microcrystallinity in polyphosphazenes can be met in only one set of circumstances—when only one type of side group is present and when those side groups are small or fairly rigid. When two or more different side groups are present the macromolecules usually lack the necessary symmetry and regularity. This is because the substitutive mode of synthesis employed for the majority of polyphosphazenes does not allow sufficient control over the stereoregularity. Hence, most mixed-substituent polyphosphazenes are amorphous. Microcrystallinity has been detected in single-substituent polymers when the side groups are F, Cl, CH_3, C_3H_7, OCH_2CF_3, OC_6H_5, and various subsituted phenoxy groups. Most aminophosphazene polymers are amorphous, perhaps because of intra- and inter-molecular hydrogen bonding.

Table 3.1 Physical Properties of Selected Polyphosphazenes Sequenced by Decreasing Glass Transition Temperature[a]

Formula	Properties	T_g (°C)	T_m (°C)
$[NP(NH\text{-}adamantyl)(OCH_2CF_3)]_n$	Glass	+180–200	—
$\{[NP(NHPh)_2]_2NC(NHPh)\}_n$ (carbophosphazene)	Glass	+112	—
$[NP(OC_6H_4C_6H_5\text{-}p)_2]_n$	Microcrystalline thermoplastic; high refractive index	+93	>350
$[NP(NHC_6H_5)_2]_n$	Glass	+91	—
$\{[NP(NHPh)_2]_2NS(O)(NHPh)\}_n$ (thionylphosphazene)	Glass	+82	—
$[N_3P_3(OCH_2CF_3)_4C_5H_4FeC_5H_4]_n$[b]	Amber-colored glass	+61	—
$[N_3P_3(OCH_2CF_3)_4C_5H_4RuC_5H_4]_n$[b]	Glass	+51	—
$[NP(OC_6H_5)(OC_6H_4C_6H_5\text{-}p)]_n$	Glass	+43	—
$[NP(NHC_2H_5)_2]_n$	Glass; soluble in aqueous acid	+30	—
$[NP(OC_6H_5)(OC_6H_4C_6H_5\text{-}o)]_n$	Glass	+24	—
$[NP(NHCH_3)_2]_n$	Glass; water-soluble	+14	—
$[NP(OC_6H_4CH_3)(OC_6H_4CHO)]_n$	Thermoplastic	+11	—
$[NP(OC_6H_4COOEt)_2]_n$	Microcrystalline thermoplastic (films)	+7.5	127
$[NP(OC_6H_4COOH)_2]_n$	Glass; soluble in aqueous base	–4.7	—
$[NP(OC_6H_5)_2]_n$	Microcrystalline thermoplastic (films, fibers)	–8	+390
$[NP(OC_6H_5)(OC_6H_4C_2H_5)]_n$	Elastomer	–10[c]	[c]
$(NPBr_2)_n$	Leathery material; hydrolytically unstable	–15	—
$[NP(OCH_2C_6H_5)_2]_n$	Elastomer	–31	—
$[(NPCl_2)_2N(S)(Cl)]_n$ (thiophosphazene)	Elastomer	–40	—
$[NP(O(CH_2)_8CH_3)_2]_n$	Elastomer.	–56	—
$\{[NP(OCH_2CF_3)_2]_2\text{-}NP(Me)(CH_2SiMe_2OSiMe_3\}_n$	Elastomer	–59	
$[NP(OCH_2CF_3)(OCH_2(CF_2)_x\text{-}CF_2H)]_n$	Elastomer	–60[c]	—
$[N_3P_3(OCH_2CF_3)_x(CH_2SiMe_3)]_n$	Elastomer	–61	—
$[N_3P_3(OCH_2CF_3)_5(CH_3)]_n$	Elastomer	–63	—
$[NP(OCH_2CF_3)_2]_n$	Microcrystalline thermoplastic; (films, fibers)	–66	+242[d]
$(NPCl_2)_n$	Elastomer; hydrolytically unstable; macromolecular intermediate	–66	–7.2(+39)[e]
$\{NP(OCH_2CF_3)_2\text{-}NP[NP(OCH_2CF_3)_3]_2\}_n$ (phosphazo)	Elastomer	–70	—
$[NP(OCH_3)_2]_n$	Elastomer	–76	—
$[NP(OC_2H_5)_2]_n$	Elastomer	–84	—
$[NP(OCH_2CH_2OCH_2CH_2\text{-}OCH_3)_2]_n$(MEEP)	Water-soluble elastomer	–84	—
$(NPF_2)_n$	Elastomer; hydrolytically unstable	–96	–68 –40
$[NP(OC_3H_7)_2]_n$	Elastomer	–100	—
$[NP(OCH_2CH_2CH_2CH_3)_2]_n$	Elastomer	–105	—

[a] For a more comprehensive list, see reference 1.
[b] Ferrocenyl polymer (**3.63**), where OR = OCH_2CF_3.
[c] Varies with ratio of side groups.
[d] Complex melting phenomena.
[e] For the stretched polymer.

3.10.3 Changes in Solid-State Morphology

In addition to the usual physical property transformations that accompany temperature changes near the T_g and T_m, certain polyphosphazenes undergo morphological transitions at temperatures *between* the T_g and the T_m. These are the so-called mesomorphic or liquid crystalline transitions (T_1, T_2, T_3, etc.) that reflect changes in chain conformation or chain packing and which become manifest in softening or partial melting, often in a complex way. Considerable work on these transitions has been carried out by Magill and coworkers, particularly on the polymers $[NP(OCH_2CF_3)_2]_n$, $[NP(OPh)_2]_n$, and various halogen-substituted phenoxy derivatives.[139–141] The compexity of the situation is illustrated by the behavior of the trifluoroethoxyphophazene polymers shown in Figure 3.11. In practical terms, the presence of mesomorphic phases often means that a polymer can be fabricated thermally at temperatures below the T_m. It also means that the strength of a fiber or film may decrease dramatically at temperatures well below T_m.

3.10.4 Hydrophobic versus Hydrophilic or Water-Soluble

The phosphazene backbone itself appears to be hydrophilic, due mainly to the presence of the nitrogen lone-pair electrons and their ability to form hydrogen bonds to water molecules. However, the overall hydrophilic or hydrophobic character is determined by the side groups and by the degree to which they shield the skeleton.

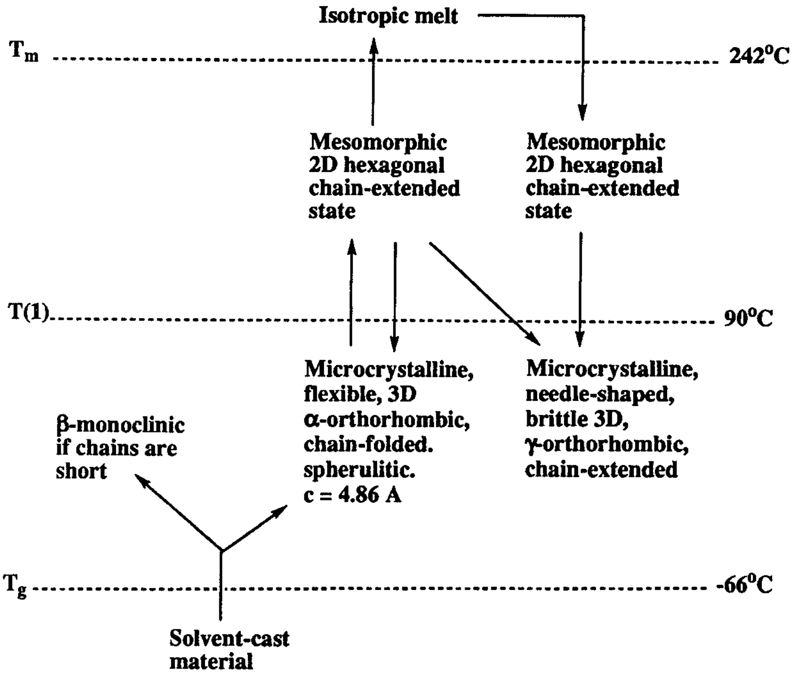


Figure 3.11 The complex quasi-crystalline transformations that occur when $[NP(OCH_2CF_3)_2]_n$ is heated or cooled. Derived from the work of Magill, Kojima, et al.

For example, side groups such as -$NHCH_3$, -$OCH_2CH_2OCH_2CH_2OCH_3$, glucosyl, and glyceryl, which are themselves hydrophilic, generate solubility of the polymer in water. Methyl side groups are sufficiently small that they do not shield the backbone nitrogen atoms: thus, methylphosphazene polymers are hydrophilic without being water soluble. On the other hand, side groups such as -OCH_2CF_3 or -OC_6H_5, that are both hydrophobic and large enough to shield the skeleton, generate strong water repellency (Figure 3.12), and confer solubility in specific organic solvents. For example, the polymer with trifluoroethoxy side groups is soluble in acetone, tetrahydrofuran, or ethyl acetate. The phenoxy derivative in soluble in hot, aromatic hydrocarbons. The ability to tailor the hydrophobic or hydrophilic character is vital if the polymers are to be used in biomedical applications (see later), while insolubility in hydrocarbons is important if the material is to be used for seals or O-rings in aircraft or automobiles.

3.10.5 Water-Stable versus Water-"Erodible"

Until recently, polymers that were unstable to water were considered to be unworthy of further consideration. Today it is recognized that such materials can be immensely valuable for use in biomedical applications, especially if the products of hydrolysis are non-toxic.

Most poly(organophosphazenes) are stable to water. Only a selected few are not. These include polymers with amino acid ester side groups, and species with imidazolyl, glyceryl, or glucosyl side units. These will be discussed later.

3.10.6 High-T_g versus Low-T_g Polymers

The side group characteristics needed to move the T_g up or down the temperature scale have been mentioned earlier. The data shown in Table 3.1 illustrate these principles for a number of different side groups.

3.10.7 Materials Structure Imposed by Side-Group Stacking

In crystals that are formed from small molecules, it is often found that large, flat molecules stack together like a pile of plates or saucers. This stacking imposes considerable order and can generate unusual optical or electrical properties.

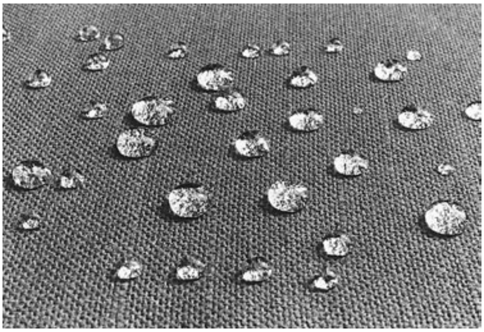
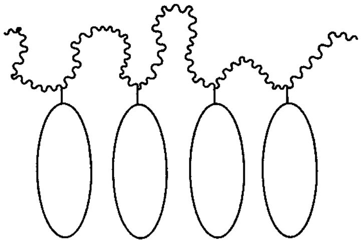


Figure 3.12 Illustration of the extreme hydrophobicity of the surface of poly[*bis*(trifluoroethoxy)phosphazene]. In this example, a cotton textile material has been impregnated with the polymer. Water droplets do not wet the surface.

If a large, flat side-group unit is attached to a flexible polymer chain, the same phenomenon may occur. In fact the tendency of the side units to form stacks may overwhelm the tendency of the chain to adopt its own preferred conformation (**3.72**). In practice, a flexible "spacer group" is usually required to decouple the motions of the side groups from the thermal motions of the chain. In some systems, side groups on neighboring chains may interleaf to form intermolecular stacks. The phenomenon of polymer liquid crystallinity can arise when side-group stacking or colinear orientation occurs.



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It will be shown in later sections that side groups such as aromatic azo or biphenyl units generate liquid crystallinity; metal phthalocyanines and tetracyanoquinodimethane generate electroactive domains; and polyaromatic units such as naphthyl or anthracene groups alter the physical properties markedly as they attempt to align their molecular axes or form stacks of side groups.

In the following sections, examples will be given of how structure–property correlations of these types have been used to make materials that are useful in technology or medicine.

3.11 Applications of Polyphosphazenes

3.11.1 Advanced Elastomers

From information presented earlier in this chapter, it will be clear that three types of molecular structures in polyphosphazenes are known to give rise to rubbery or elastomeric properties. These are summarized in Table 3.1. First, if the side groups are single atoms, such as fluorine, chlorine, or bromine, the inherent flexibility of the backbone dominates the materials' flexibilty and gives rise to elastomeric character. Unfortunately, the polymers $(NPF_2)_n$, $(NPCl_2)_n$, and $(NPBr_2)_n$ are slowly hydrolyzed in contact with atmospheric moisture. Hence, they are of interest as reaction intermediates but not as usable materials.

The second group of elastomeric polyphosphazenes are those in which the organic side groups are sufficiently flexible that they can readily undergo "avoidance" motions as the skeletal bonds twist. Thus, the side groups impose little or no additional barrier to the twisting motions of the skeleton. Linear side groups such OCH_3, OC_2H_5, OC_3H_7, OC_4H_9, $OCH_2CH_2OCH_3$, or -$OCH_2CH_2OCH_2CH_2OCH_3$ fall into this category. Side groups such as these probably assist polymer chain motions in another way also.

Being themselves capable of assuming different conformations and shapes, they do not fill the available space in the most efficient manner. Thus, molecular voids of "free volume" exist and this space provides freedom for movement of the polymer chains. The greater the free volume the greater the material's flexibility. The elastomers in this class are, in general, stable to water.

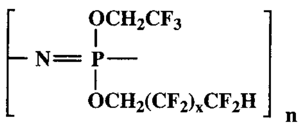
The third group of polyphosphazene elastomers includes species in which two or more different alkoxy, aryloxy, or organosilicon units are attached to the polymer chains.[60–66] The principle behind the design of elastomers of this type is that the random distribution of two or more different side groups reduces the tendency for interchain alignment and crystallinity, and also (if the side groups are of different dimensions) generates free volume that assists macromolecular reorientation. Three main classes of elastomers that fulfill these requirements are known: -mixed-substituent fluoroalkoxyphosphazenes; mixed-substituent aryloxyphosphazenes; and polymers that contain both organosilicon and alkoxy or aryloxy cosubstituent groups. These will be considered in turn.

The first polyphosphazenes to be developed commercially were polymers with two different types of fluoroalkoxy side groups attached to the same chain.[142–145a] A typical example is shown in **3.73**. Polymer **3.73** has a more complicated structure than is implied by the illustration. The polymer is synthesized by the reaction of a mixture of CF_3CH_2ONa and $CHF_2(CF_2)_xCH_2ONa$ with poly(dichlorophosphazene). This means that the two nucleophiles *compete* for replacement of the available chlorine atoms, a process that could lead to a random distribution of side groups, but could also generate repeating units in which the phosphorus atoms bear two of the same side groups.

Elastomers of this type are usually cross-linked during fabrication, and often contain "fillers" such as carbon black or iron oxide to reduce the "compliance" of the elastomer (i.e. to provide a greater resistance to deformation). Such materials are depicted in Figure 3.l. They are used in technology because of their flexibility and elasticity at low temperatures (–60 °C), their resistance to hydrocarbon solvents, oils, and hydraulic fluids, and their fire resistance.[145] For these reasons, they are utilized in aerospace and advanced automotive applications. Some interest exists in their development as inert biomaterials, mainly because of their surface hydrophobicity and consequent biocompatibility.

The mixed-substituent aryloxyphosphazenes are typified by the stucture shown in **3.74**, where R is an alkyl group.[144] Again, the polymers probably contain some repeating units with a single type of side group. The glass-transition temperatures of these materials are not as low as for the fluoroalkoxy derivative. These polymers are of interest mainly as non-flammable, sound- and electrical-insulating materials, often in the form of an expanded foam rubber (Figure 3.2).

The final class of mixed-substituent elastomers is still at the stage of laboratory investigation, rather than manufacturing. They comprise a group of polymers such as **3.75** or **3.76** that contain organosilicon side groups as cosubstituents.[146,146a] These polymers are prepared by the initial polymerization of a cyclophosphazene that has one organosilicon side group per ring, as illustrated earlier in reaction (15), followed by replacement of the halogen atoms in the polymer by reaction with sodium trifluoroethoxide. Structures of this type are interesting because they are hybrids of polyphosphazenes and organosilicon polymers. Their hydrophobicity and membrane properties are of special interest.



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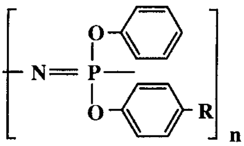

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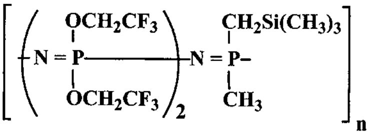

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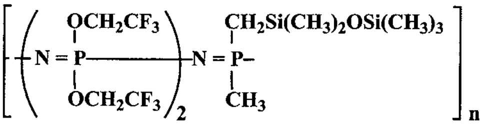

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3.11.2 Passive Membranes for Gas and Liquid Separations

Membranes are thin polymeric films that may permit the faster diffusion of some molecules than of others. Thin films of polymers are widely used for the separation of gases and for liquid-phase separations (dialysis). Because of the ease of property tuning, polyphosphazenes are of great interest for these types of applications, although only a few examples have yet been investigated.

Aryloxy-substituted polyphosphazenes have received the most attention as gas separation membranes.[147–152] For example, $[NP(OPh)_2]_n$ membranes show promise for the removal of sulfur dioxide from nitrogen at 30 °C or for removing methylene chloride or chloroform from air. Membranes prepared from the trifluoroethoxy-substituted polymer, $[NP(OCH_2CF_3)_2]_n$, have a high permeability to carbon dioxide, hydrogen, and oxygen, and this could be useful in a variety of applications including underwater breathing apparatus or fuel cell technology.[153–155]

Liquid-phase separations can be carried out with membranes produced from several different classes of polyphosphazenes. An example membrane prepared from $[NP(NHC_4H_9)_2]_n$ is shown in Figure 3.13. The polymer, $[NP(OCH_2CF_3)_2]_n$, can be employed to concentrate alcohols, because the alcohol diffusion rate is much faster than that of water.[156]

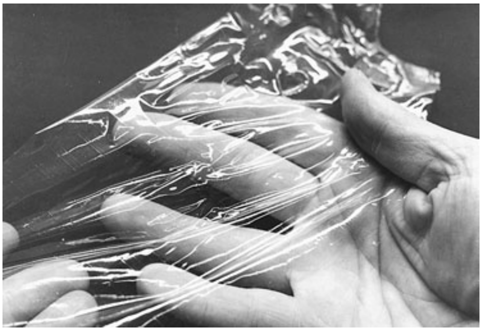
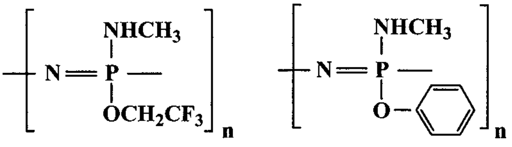


Figure 3.13 A thin film of poly[*bis*(butylamino)phosphazene] fabricated by solution casting for membrane experiments.

Such materials are known as semipermeable membranes. They are essential components of nearly all living things, and the development of new materials of this type is an important component of biomedical research. The control of diffusion of molecules through a membrane can be accomplished by variations in the hydrophilicity of the polymer molecules that constitute the membrane. As in biological membranes, hydrophobic molecules are more likely to pass through the hydrophobic domains of a synthetic membrane than through the hydrophilic regions, and vice versa.

It will be fairly obvious from the earlier parts of this chapter that the synthesis methods used in polyphosphazene chemistry offer almost unique opportunities for modifying and fine tuning the surface and bulk properties of a polymer. For example, variations in the ratios of hydrophilic and hydrophobic side groups can generate a whole range of "amphiphilic" properties that may be useful in membrane design and technology. The following example illustrates some of the opportunities that exist in this area of research.[157]



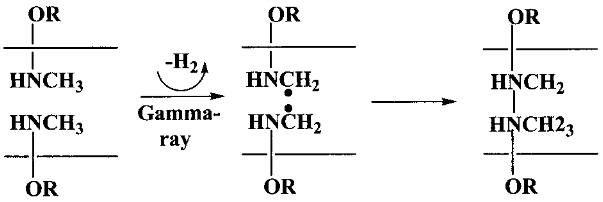
3.77 **3.78**

The methylamino group is hydrophilic. Trifluoroethoxy and phenoxy groups are hydrophobic. Thus, by varying the ratios of methylamino to trifluoroethoxy or phenoxy in structures such as **3.77** or **3.78** over the range of 0–100% of each type of group, it is possible to vary the surface properties and the semipermeable membrane behavior.

The methylamino single-substituent polymer has a surface contact angle of 30° or less, whereas the trifluoroethoxy and phenoxy single-substituent polymers have values in the range of 100–107°. Although a rough relationship exists between side-group ratio and surface contact angle, the values can be distorted by the fact that hydrophilic side groups will be concentrated at the polymer surface if that surface was formed in contact with a hydrophilic material such as glass. Moreover, measured contact angles may change over time as side groups that were concentrated at the surface when the surface was formed become buried by molecular motions as the polymer is stored. The high chain mobility of the phosphazene skeleton tends to accelerate this process.

The semipermeability behavior of a polymer film can be measured by equipment that permits measurements of the diffusion of a small-molecule dye through the membrane. In the phosphazene systems investigated, the rate of diffusion varied with the polymer side group ratio. A typical polymer with roughly 50% of the side groups as methylamino and 50% as trifluoroethoxy showed a faster transmission of dye molecules in water than did standard cellulose dialysis tubing.

Membrane design and fabrication requires more optimization than the synthesis of the right type of polymer. For example, those phosphazene polymers that contained the highest ratios of methylamino groups were too brittle to be used as membranes (because of the high glass-transition temperatures) and too soluble in aqueous media. However, the polymers could be made insoluble in water by radiation cross-linking as shown in reaction (54).



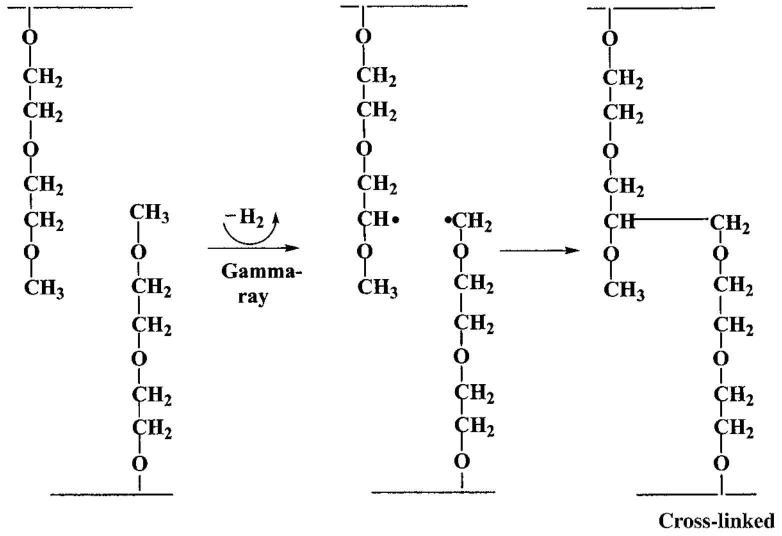
(54)

$R = CH_2CF_3$ or C_6H_5

3.11.3 Responsive Membranes

A responsive membrane is one in which the permeability to a dissolved solute can be altered by changes in temperature, pH, ion strength, light intensity, electrical current, magnetic field, and so on. A major interest is the ability to use the membrane as a "switch" to turn on or turn off the flow of molecules in response to changes in the "environment." Obvious examples exist in biomedical technology, where the release of a drug from an implanted device needs to be controlled automatically in response to changes in the temperature or biochemistry of a patient.

Polyphosphazene hydrogels have been investigated intensively for this type of application. Their behavior as membranes is based in the following facts. First, phosphazenes with alkyl ether side chains, such as $-OCH_2CH_2OCH_2CH_2OCH_3$ units, can be cross-linked easily by UV or gamma radiation (reaction (55)).[158–160] Cross-linking converts a polymer that is soluble in water to one that swells by absorbing water, but does not dissolve. It forms a hydrogel (Figure 3.14). Second, polymers of this type have what is known as a lower critical solution temperature (LCST), where the polymer is soluble below the LCST but precipitates above that temperature. The corresponding (cross-linked) hydrogels are swollen by water below the LCST but contract above that temperature. Depending on the type of alkyl ether side groups that are present, the LCST



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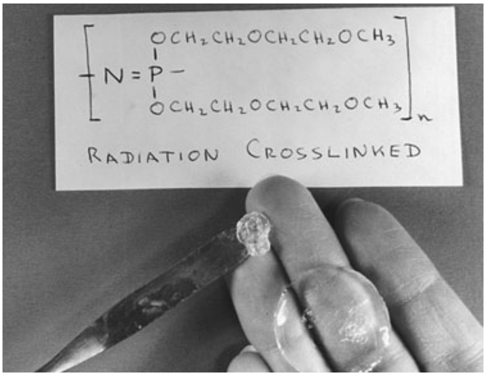


Figure 3.14 Lightly cross-linked poly[*bis*(methoxyethoxyethoxy) phosphazene] (small pellet of elastomer on the tip of the spatula) absorbs water to form a hydrogel (lower right).

can range in polyphosphazenes from 30 °C to 65 °C. The most interesting ones are those with an LCST near 38 °C (human body temperature). Third, cosubstituent side groups that bear carboxylic acid functional units, such as -OC_6H_4COOH, make the hydrogel pH-responsive.[161] The gels expand at high pH and contract at low pH. A contracted gel membrane prevents the transmission of solvent and solute molecules. An expanded gel allows their diffusion. This is illustrated in Figure 3.15.

3.11.4 Membranes from Polymeric Solid Ionic Conductors

Two types of solid ionic conductors are of special interest—those in which metallic cations such as lithium ions can be transported across the polymer membrane, and others in which protons can move from one side of the membrane to the other. The first

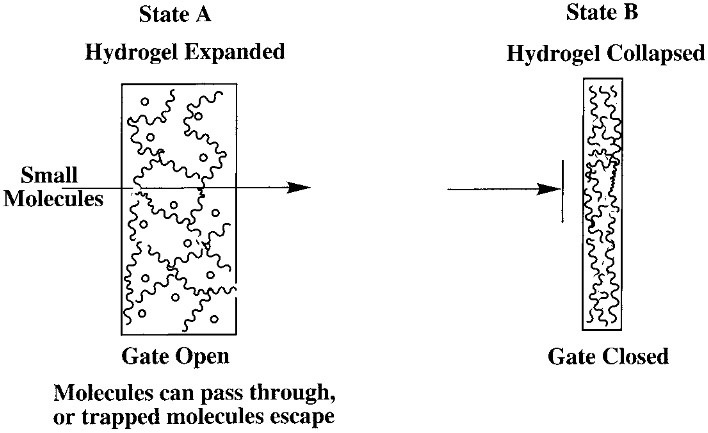
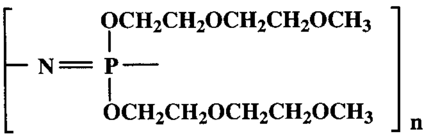


Figure 3.15 Illustration of the use of a responsive hydrogel to control the passage of small molecules through a membrane. From reference 1.

type is important for use as the electrolyte in advanced rechargeable lithium batteries. Proton-conducting membranes are crucial components in fuel cells. Specific polyphosphazene have shown promise for both types of applications.

Polyphosphazenes as Metal Ion Conductors

One group of polyphosphazenes has received considerable attention because of their advantages for lithium ion conduction. These are polyphosphazenes with oligo-ethyleneoxy side groups. They are characterized by their high molecular flexibility and their ability to coordinate weakly to lithium and other monovalent ions. A well-known example is poly[*bis*(methoxyethoxyethoxy)phosphazene) (**3.79**), also known by the acronym "MEEP" (MethoxyEthoxyEthoxyPhosphazene). Numerous other polyphosphazenes with different alkyl ether side groups and different architectures have also been studied as ionic conductors.



3.79

Polymers such as MEEP function as *solid* solvents for salts such as lithium triflate ($LiSO_3CF_3$), lithium trifluorosulfonimide, or silver triflate. The widespread interest in polymer/dissolved salt system membranes is a consequence of their ability to function as ionic conductors of electricity. Solvation of the ions (particularly the cations) by the oxygen atoms in the side groups, favors ion-pair separation. Moreover, if the polymer chains are sufficiently flexible (and if sufficient free volume exists), the cations can be transferred from chain to chain as the macromolecules undergo thermal motion. This is illustrated in Figure 3.16. If an electric current is applied, the cations will migrate toward the negative electrode and the anions toward the positive electrode.[1,162,163]

This principle is utilized in the design and construction of experimental lightweight, high energy density rechargeable lithium batteries, as illustrated in Figure 3.17. In theory, there is almost no limit to the size of batteries constructed in this way since the solid electrolyte component can be solution-cast as a film. Until recently, poly(ethylene oxide), $(CH_2CH_2O)_n$, was the prototype polymer for such applications. However, poly(ethylene oxide) is microcrystalline, and ionic conduction in the amorphous regions is interrupted by the microcrystalline domains. For this reason, this polymer must be heated to nearly 100 °C before a high ionic conductivity can be obtained.

On the other hand, polyphosphazene **3.79** and its variants are non-crystalline. Their ionic conductivities at room temperature are 1,000 times or more greater than that of poly(ethylene oxide).[164–166] For battery type applications, **3.79** must be cross-linked lightly to prevent slow liquid-like flow, but this can be accomplished by radiation techniques without lowering the conductivity. An analogous type of polymer, with a polysiloxane backbone and oligoether side groups, is being studied for similar applications.

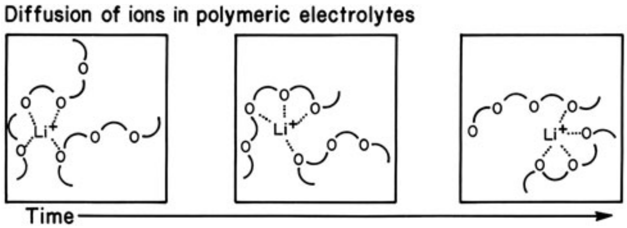


Figure 3.16 Ionic electrical conductivity for solutions of lithium triflate in solid poly[*bis*(methoxyethoxyethoxy)phosphazene] ("MEEP") is believed to occur following coordination of the etheric side groups to Li+ ions, cation-anion separation, ion transfer from one polymer to another as the polymer and side groups undergo extensive thermal motions. From Shriver and Farrington, *Chem. & Eng. News,* 1985, 42–57 (May 20). Reprinted by permission of the American Chemical Society.

Several other types of polyphosphazenes with different architectures have been studied for potential battery applications. These include polyphosphazenes with branched alkyl ether side chains[167,168] Other systems studied include hybrid macromolecules in which an organic polymer chain bears cyclic trimeric phosphazene side groups (**3.16**), which themselves bear alkyl ether side units,[169,170] or comb-type organic polymer chains (**3.15**) with MEEP-type pendent side chains.[171] Block copolymers of MEEP with poly(ethylene oxide) have also been examined.[172,173] The highest room temperature conductivities achieved by these solid electrolyte systems is in the range of 10^{-4} S/cm, which is roughly an order of magnitude less than the value required for many applications. However, the conductivities of all these systems can be enhanced by the addition of small quantities of coordinative organic liquids such as propylene carbonate, which boost the conductivity into the 10^{-3} range.[174–176] These "gel electrolytes" offer some significant advantages over solvent-swelled poly(ethylene oxide) systems because the amount of flammable organic solvent needed to achieve respectable conductivities is much less. The exact mechanism of ion conduction in both the solvent-free and the gel polyphosphazene systems is a subject of ongoing interest.[177–180]

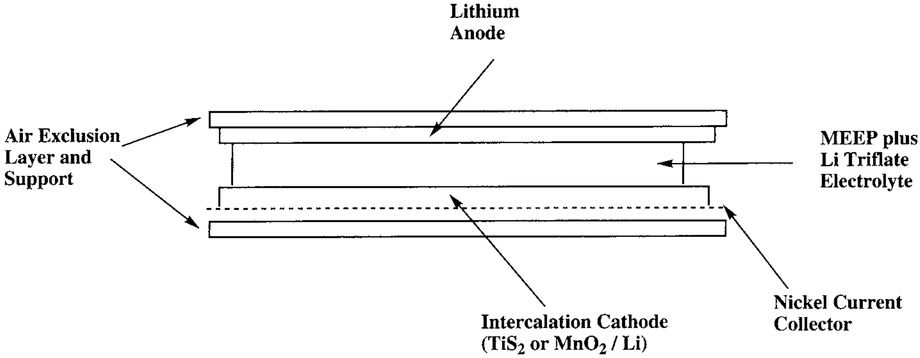


Figure 3.17 Cross-sectional diagram of a thin film rechargeable lithium battery based on the conductivity of lithium triflate in solid poly[*bis*(methoxyethoxyethoxy)phosphazene].

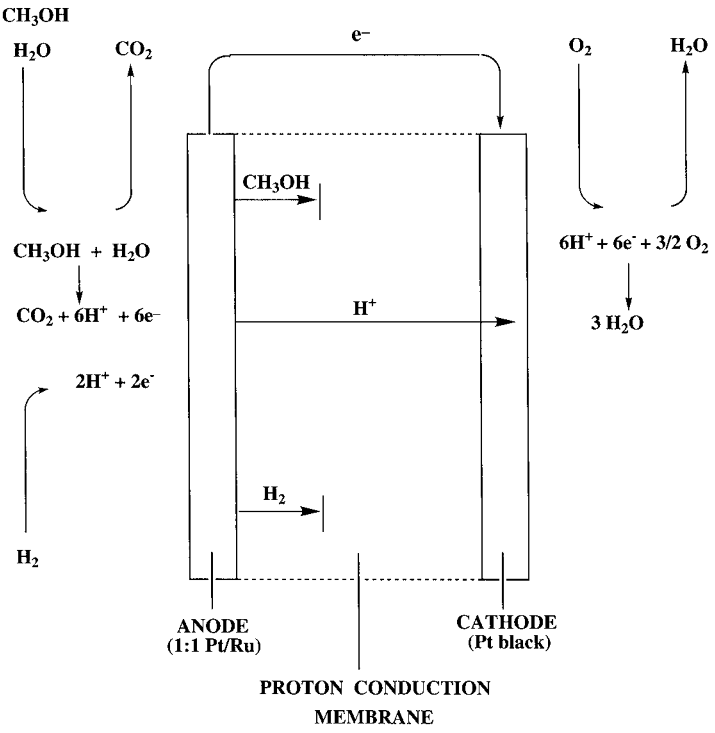
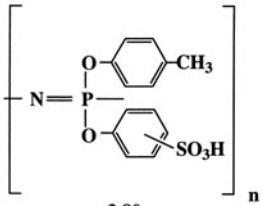


Figure 3.18 Schematic diagram of a polymer electrolyte fuel cell based on a proton-conductive polymer membrane.

Proton-Conducting Polyphosphazenes

The structure of a polymer electrolyte fuel cell is shown in Figure 3.18. Fuel in the form of hydrogen or methanol is converted to electrons and protons by the catalyst on the anode. The electrons move through the external circuit and the load to the cathode. The protons must be transported through polymer membrane to the cathode where they react with oxygen to form water. Very few polymers are known that can transport protons efficiently, especially at high temperatures, and can survive the aggressive chemical reactions that take place near the cathode. A key requirement for a polymer electrolyte fuel cell membrane, in addition to chemical and heat stability and proton conduction, is its resistance to transmission of the fuel to the cathode. Existing commercial membranes, such as Nafion, readily transmit methanol and this is one of the major barriers to the development of direct methanol fuel cells.

Three examples of polyphosphazenes that function as proton conductors are shown in **3.80–3.82**.[181–185] All three are aryloxyphosphazenes with acidic functional groups on the aryl rings. Their performance in operating fuel cells is comparable to that of Nafion, but they are much more resistant to methanol crossover. The sulfonimide derivative (**3.82**) functions as a proton conductor at higher temperatures than Nafion, and this is an advantage for future developments.



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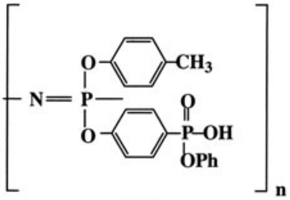
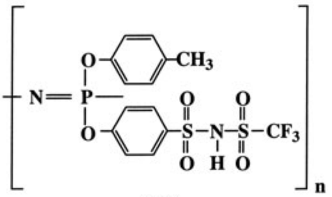


3.81



3.82

3.11.5 Fibers, Films, and Special Surfaces

Fibers

The main requirements for good textile fiber are (a) a T_g below room temperature (to provide flexibility at normal temperatures), together with (b) microcrystallinity to provide strength, orientability, and (sometimes) ease of fabrication by melting. The classical organic polymers used for fibers (Nylons, polyesters, and polyolefins) generally have these characteristics.

As discussed earlier, microcrystallinity in polyphosphazenes can generally be achieved only with single-substituent polymers such as those with OCH_3CF_3, OPh, or OC_6H_4R-*p* side groups, although a few mixed-substituent derivatives are also crystalline. Many of these polymers are film- and fiber-forming materials (Figure 3.3). They can be fabricated more easily by solution-casting or solution-spinning than by melt-fabrication techniques. This is because the microcrystallites melt at temperatures that are so high (sometimes over 250 °C) that the polymers begin to depolymerize as they are melt-fabricated.

Films and Surface Coatings

Many polyphosphazenes form strong films and membranes when solutions are spread on a flat surface and the solvent is allowed to evaporate. Some of these films have special properties such as resistance to UV radiation, and are thus of interest as coatings for solar cells, aircraft, or space craft. The polymer $[NP(OCH_2CF_3)_2]_n$ and related mixed-substituent derivatives have been studied from this viewpoint.[1]

Surface coatings require strong adhesion to the surface, often coupled with cross-linking of the polymer. Cyclolinear and cyclomatrix phosphazenes have been investigated intensively for these applications. In general, the fiber, film, and coatings technology of polyphosphazenes is at an early stage of development, with laboratory studies and patents more evident than manufacturing.

Films with Special Surfaces

As discussed earlier, polyphosphazene surfaces can be modified by reactions that change the side groups in the surface region without affecting the bulk material. A striking example of this is the generation of an adhesive surface on one or both faces of films of $[NP(OCH_2CF_3)_2]_n$ by treatment with aqueous base in the presence of Bu_4NBr (reaction (29)). This provides a means for the adhesion of protective films of this polymer to

other materials. Another example is the treatment of $[NP(OCH_2CF_3)(OCH_2(CF_2)CF_2H)]_n$ adhesive elastomer with $NaOCH_2(CF_2)CF_2F$ to generate a non-adhesive surface. Surface reactions are available to alter the interfacial properties of nearly all polyphosphazenes.

3.11.6 Polyphosphazenes as Biomedical and Biotechnology Materials

Background

The use of synthetic polymers in medicine and biotechnology is a subject of wide interest. Polymers are used in replacement blood vessels, heart valves, blood pumps, dialysis membranes, intraocular lenses, tissue regeneration platforms, surgical sutures, and in a variety of targeted, controlled drug delivery devices. Poly(organosiloxanes) have been used for many years as inert prostheses and heart valves. Biomedical materials based on polyphosphazenes are being considered for nearly all the uses mentioned above.

A significant advantage of poly(organophosphazenes) over nearly all other biomedical polymers is the ease with which different organic side groups can be linked to the polyphosphazene chain. Thus, by changing the types of side groups present, it is possible to generate virtually any combination of properties needed for a particular biomedical application, including the ability to hydrolyze ("erode") in the body to non-toxic small molecules that can be metabolized or excreted.[1] Some polyphosphazenes with specific combinations of properties can be used in several different biological applications. Thus, in the following sections the discussion is organized around the way in which specific *properties* are generated rather than around the applications. The appropriate applications will mentioned as they arise.

Hydrophobic, Bioinert Polyphosphazenes

Some of the most useful biomaterials in use at the present time are inert, hydrophobic classical organic polymers, such as polyethylene or poly(tetrafluoroethylene) (Teflon or GoreTex). Much of the utility of these materials stems from their hydrophobic surface character which minimizes the "foreign body" interactions that normally occur when non-living materials are implanted in contact with living tissues, including blood. Another advantage is that their hydrophobicity discourages bacterial or fungal colonization, which is a serious problem with implanted biomedical devices. A hydrophobic surface also has some advantages for the prevention of protein deposition and the facilitation of endothelial cell overgrowth. However, it should be noted that no known synthetic material is truly bioinert.

Three different types of poly(organophosphazenes) are being studied as bioinert materials, and these are typified by the structures shown earlier as **3.29**, **3.31**, **3.73**, and **3.76**. All are hydrophobic polymers, with the hydrophobicity being generated by the fluorocarbon, aryl, or organosilicon side groups. Surface hydrophobicity is estimated by the contact angle formed when a drop of water is placed on the surface of a polymer. Low contact angle values are found when the droplet interacts with and wets the surface. High contact angles indicate a hydrophobic surface (Figure 3.12). Poly(tetrafluoroethylene) has a contact angle of 107°.

All the polyphosphazenes shown have high contact angles in the region of 100–107°. The fluoroalkoxy and aryloxy derivative (**3.29**, **3.73**, and **3.31**) have been

studied by means of implantation tests in animals and have shown minimal tissue response.[186] Thus, hydrophobic polyphosphazenes of these types are good candidates for use in cardiovascular replacements (heart pumps, heart valves, or blood vessel prostheses), or as coatings for pacemakers or other implantable devices.

Biostable Polymers with Hydrophilic or Bioactive Surfaces

Not all implantable biomaterials have hydrophobic surfaces. Some are deliberately designed to stimulate tissue adhesion or infiltration or to generate a biochemical response. Such polymers are either inherently hydrophilic and chemically inert or they have bioactive agents on the polymer surface. Many aminophosphazene polymers are intrinsically hydrophilic because the amino side groups can form hydrogen bonds with water molecules. Examples include polymers with CH_3NH-, C_2H_5NH-, C_3H_7NH-, and so on, side groups. Quaternization of surface amino groups can increase the hydrophilicity. In addition, certain alkoxy side groups such as OC_2H_5, $OCH_2CH_2OCH_3$, or $OCH_2CH_2OCH_2CH_2OCH_3$ or aryloxy units with OH or COOH substituent groups also generate hydrophilic surface character. In some of these cases the polymers are so hydrophilic that they may dissolve in water, but this tendency can be counteracted by cross-linking or by the presence of hydrophobic cosubstituent units.

As discussed in an earlier section, the chemistry exists to convert hydrophobic polyphosphazenes to materials with hydrophilic surfaces. Hydrogels of MEEP (**3.79**) have been radiation grafted to the surfaces of hydrophobic polymers to generate highly hydrophilic interfaces, and these systems have the advantage that the interior of the polymer retains its hydrophobicity and other properties, and only the surface layers are changed.[187,188]

Biological compatibility to blood or other tissues often depends on surface charge or the presence of ionic groups. One way in which such surface structure can be generated is by sulfonation of the surface of an aryloxyphosphazene by treatment with concentrated sulfuric acid as discussed earlier (reaction (32)). The reaction conditions must be controlled carefully to prevent dissolution of the polymer in strong acid, and subsequent chain cleavage. But, under the right conditions, an outer layer of sulfonated aryloxyphosphazene units is formed. This change converts a hydrophobic surface (contact angle, 101°) to a hydrophilic surface (contact angle, 0°) in one simple step. The influence of this transformation on blood and tissue compatibility is still being investigated, but it is known that similar changes in the surface character of organic polymers brings about a dramatic improvement in blood compatibility.

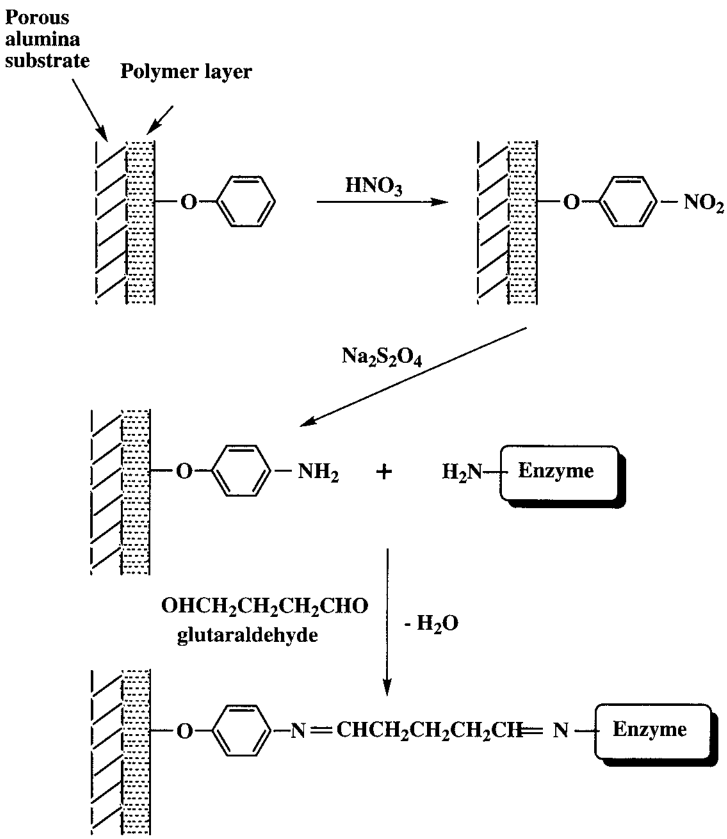
Other surface modification reactions that are relevant to biological studies include the binding of the blood anticoagulent, heparin,[189] and of dopamine[190] to polyphosphazene surfaces. The heparin immobilization brought about a five-fold increase in the coagulation time of blood, and the immobilized dopamine generated the same response in rat pituitary cells as did free dopamine.

Surface-functionalized polymers are also of interest for uses in biochemical reactors, and biomedical sensors. The immobilization of enzymes on a polymer surface is an important example. Numerous reasons exist for attempting to immobilize enzymes on the surfaces of polymers. For one thing, immobilization often enhances the length of time over which the protein maintains its catalytic activity, compared to the same

enzyme free in solution. Second, immobilization facilitates the separation of the enzyme from the products of an enzyme-induced reaction, for example, by using the polymer/enzyme conjugate as the stationary phase in a continuous-flow reactor. Third, it may be possible to immobilize several different enzymes on the same surface so that the products of a reaction induced by one enzyme become the starting materials for a transformation catalyzed by the second, and so on. For all such processes it is usually advantageous to use a form of the immobilization polymer that provides the greatest possible surface area. For this reason, small particles of the polymer are normally used.

Enzymes have been linked covalently to the surface of a poly[*bis*(aryloxy)phosphazene].[191] In the system to be described, the high surface area was ensured by depositing a thin film of poly[*bis*(phenoxy)phosphazene] (**3.31**) on to the surface of highly porous small particles of alumina powder. Provided the deposition of the polymer is controlled carefully so as not to block the microscopic pores, an enormous surface area of polymer can be generated (see Figure 3.19). Surface chemistry on the polymer was then carried out according to the reactions shown in reaction sequence (56).

Thus, surface nitration generated nitrophenoxy units at the interface. Reduction with dithionite then converted the nitro groups to amino functions. At this stage a variety



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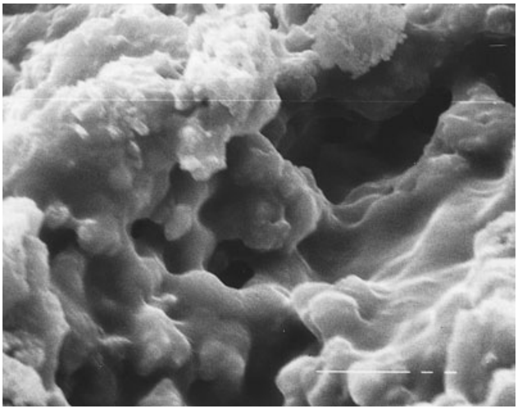


Figure 3.19 Scanning electron micrograph of the surface of a porous alumina particle covered with poly[*bis*(phenoxy)phosphazene]. The polymer was then surface nitrated, reduced, and the reactive sites used for coupling to enzymes. From Allcock and Kwon, reference 191.

of methods were used to couple the enzymes trypsin or glucose 6-phosphate dehydrogenase to the surface. The most effective method was to use glutaric dialdehyde ($OHC(CH_2)_3CHO$) as a coupling agent. This reagent reacts with both the amino groups on the surface and amino groups on the enzyme to complete the immobilization process.

A large part of the enzymic activity was retained after immobilization, as illustrated in Figure 3.20. Moreover, packing of the conjugate particles into a chromatography-type column allowed the construction of a continuous flow reactor. Figure 3.20 illustrates that the enzyme molecules continued to catalyze their reactions for long

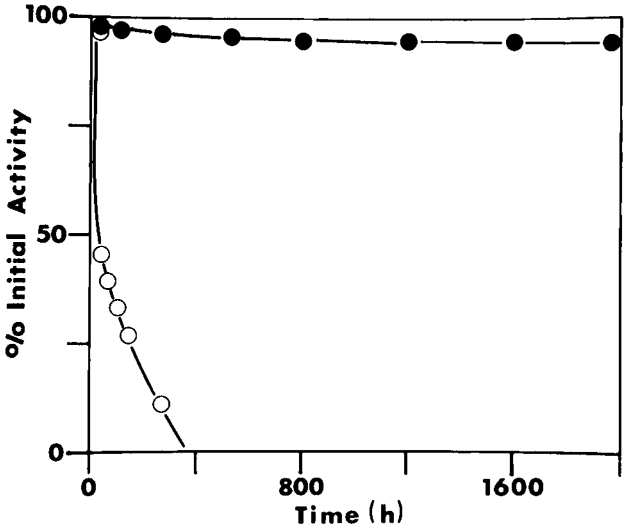


Figure 3.20 Plots showing the activity of the enzyme, glucose-6-phosphate dehydrogenase as a function of time for (open circles) the free enzyme in solution and (black circles) the enzyme bound to the surface of poly[*bis*(phenoxy)phosphazene]. The polyphosphazene is an excellent surface substrate because of the stability of the polymer backbone to nitration and reduction, and the ease with which the hydrophobicity or hydrophilicity of the surface can be changed. From Allcock and Kwon, reference 191.

periods of time. Practical uses of immobilized enzymes can be foreseen not only in the biochemical and fermentation industries, but also in medical diagnostic equipment and, possibly, in the construction of the artificial liver.

Hydrogels

As discussed earlier, hydrogels can be prepared by cross-linking water-soluble polymers. When immersed in water, such materials absorb water and swell, but they cannot dissolve because of the constraints imposed by the cross-linked structure. The volume expansion is limited by the degree of cross-linking. The minimum number of cross-links required to form an insoluble matrix is approximately 1.5 per chain, and this yields a system with the maximum expansion possible without separation of the chains into a true solution. Thus, a hydrogel may be more than 95% water, yet it has structure and, in that sense, has much in common with living soft tissues.

In addition to their uses in membranes, hydrogels have many potential applications in biomedicine, ranging from materials for the construction of soft tissue prostheses or tissue-like coatings, to linings for heart valves or artificial blood vessels, and matrices that imbibe drug molecules and release them by diffusion. Additional prospective applications include their use as substrates for enzyme or antigen immobilization and as materials that favor tissue ingrowth. Some soft contact lenses and intraocular lenses are hydrogels. Hydrogels may be biostable or they may be bioerodable. Erosion can occur by hydrolysis of the chains or by cleavage of the cross-links.

The principal polyphosphazenes that have been used in hydrogels are those with linear or branched ethyleneoxy side chains, aryloxy groups with carboxylic acid substituents, or mixed-substituent polymers that bear hydrophilic methylamino side groups plus a hydrophobic cosubstituent such as phenoxy or trifluoroethoxy. Cross-linking is usually accomplished by gamma-ray irradiation or, in the case of the carboxylic acid functional species, by treatment with a di- or tri-valent cation. Here, we will consider another example based on MEEP (**3.79**), a polymer that is well suited to the "clean" method of radiation cross-linking.

Polymer **3.79** is quite sensitive to gamma-radiation induced cross-linking, due to the presence of 11 carbon-hydrogen bonds in each side group.[192–194] Thus, relatively low doses of gamma-radiation (1–2 Mrad) convert it from a water-soluble polymer to a material that imbibes water to form a hydrogel. The degree of water imbibition depends on the degree of cross-linking which, in turn, depends on the radiation dose. Hydrogels formed from this polymer are stable to water and, as discussed in an earlier section, can be used in responsive membranes. The gels also appear to be interesting candidates for use as intraocular lenses, soft tissue prostheses, or as hydrophilic coatings for biomedical devices. They can also be used as matrices for the immobilization of enzymes.

Just one example will be given here.[195] Evaporation of water from aqueous solutions of MEEP and the enzyme urease yields films that can be cross-linked by exposure to gamma rays. The cross-linked films absorb water to form hydrogels in which the enzyme molecules are trapped within the interstices of the gel network. Some of the enzyme molecules may also be covalently grafted to the polymer side groups. The immobilized enzyme retained approximately 80% of its activity for the conversion of urea to ammonia. This system can, in principle, be used for the immobilization of a wide variety of enzymes, and for their use in biochemical flow reactors, or in sensors.

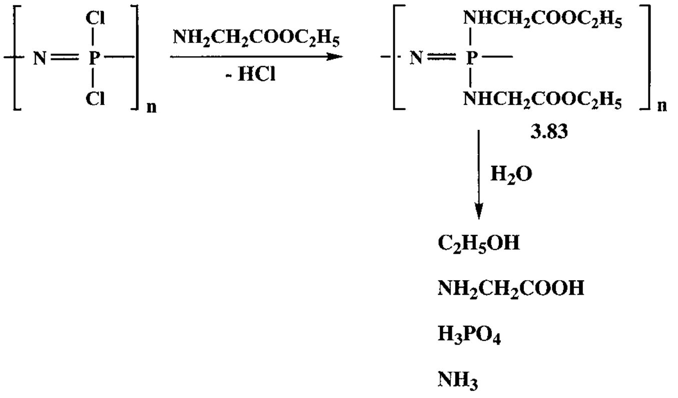
Moreover, because MEEP and its hydrogels have a lower critical solution temperature, the activity of the enzyme can be shut down by slight increases in temperature and restarted by lowering the temperature.

Bioerodible Solid Polymers

Three main uses exist for bioerodible polymers. First, they can be used as resorbable surgical sutures or staples in surgery. Second, they are of considerable interest in the field of "tissue engineering." Although the use of inert, implantable biomaterials in the human body is an important area of research, a far more attractive option is to allow the body to regrow a damaged tissue or organ using cells cultured from the patient. The idea is to produce a template in the shape of the target tissue or organ, to seed it with the patient's own cells, and to then allow cell spreading to occur to the limits defined by the boundaries of the device. Clearly, this requires the use of polymers that will, over time, decompose to non-toxic products as the process proceeds. Hydrolysis of the polymer is the normal method used for its decomposition. Bioerodible organic polymers of this kind are known, and the most common example is poly(glycolic-lactic acid), but this material hydrolyzes to acidic products which inhibit tissue regrowth. The third use for bioerodible polymers is as matrices for the slow, controlled release of drug molecules as the polymer hydrolyzes (Figure 3.21).

Specific phosphazene polymers can be designed to decompose slowly in water at the pH of many body fluids (pH 7.5) to give products that are non-toxic and are buffered to pH 7.[1,196–207] The erosion process converts a macromolecular system that has all the attributes of a polymer (strength, elasticity, ease of fabrication, ability to act as a reservoir for other molecules) to small molecules that are soluble in water and can be removed by metabolism or excretion.

The main class of bioerodible polyphosphazenes that have been developed so far are polymers with amino acid ester side groups. They are prepared by the reaction of poly(dichlorophosphazene) with the ethyl or propyl esters of amino acids such as glycine, alanine, phenylalanine, and so on (reaction (57)).[196] The ethyl or propyl *ester* of the amino acid must be used as the nucleophile in this reaction for two reasons. First, a free carboxylic acid unit would provide a second nucleophilic site that could lead to



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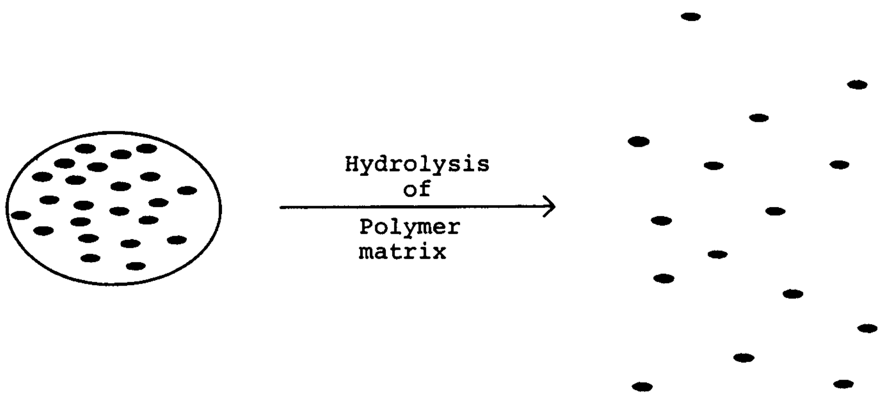
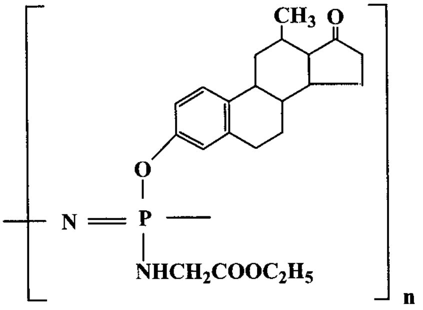


Figure 3.21 Bioerodable polymers can be used for the controlled release of pharmaceutical molecules (black elipses). Ideally, hydrolysis of the implanted matrix polymer should occur at the polymer surface only so that the drug molecules are released at a constant rate—a so-called zero-order release profile.

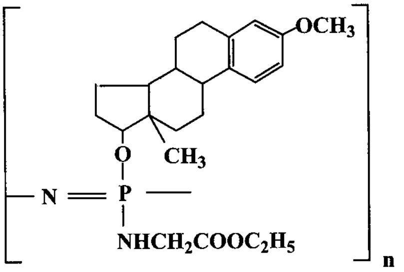
cross-linking of the polymer chains. Thus, the ethyl ester function serves as a protecting group. Second, even if the amino terminus were the only site to react, the pendent free carboxylic acid unit would induce rapid decomposition of the polymer. In fact, this is what happens once the side unit is deprotected during hydrolysis. Hence, the ester function stabilizes the polymer until it is exposed to an aqueous environment.

The utility of polymers such as **3.83** is that they are sensitive to hydrolysis at body pH and that, on hydrolysis, they yield ethanol or propanol, amino acid, and phosphate which can be metabolized, and small amounts of ammonia which can be excreted.[196] Moreover, the rate of hydrolysis depends on the type of amino acid ester used. For example, phenylalanine derivatives hydrolyze more slowly than glycine derivatives. Propyl esters retard hydrolysis compared to their ethyl ester counterparts. The mechanism of hydrolysis is quite complex and changes with variation in pH.[196,208] In near-neutral aqueous media, the ester function appears to be hydrolyzed first to deprotect the carboxylic acid units. Hydrolytic cleavage of a side-group P-N bond occurs next to release glycine. This leaves a hydroxyl group attached to phosphorus in place of the organic side group. Hydroxyphosphazenes are intrinsically unstable, and the skeletal bonds are broken rapidly by hydrolysis as degradation to phosphate and ammonia occurs.

These polymers show a great deal of promise as biomedical materials. In subcutaneous tissue compatibility experiments the polymers decompose without evidence of toxicity, irritation, or giant cell formation. They have been studied in detail for the controlled release of the antitumor agent, L-phenylalanine mustard (melphalan).[209] A development from this chemistry is the use of the bioerosion process to release drug molecules that are bound to the polymer skeleton as substituents or cosubstituents. For example, the two model steroidal structures shown in **3.84** and **3.85** have been used, along with ethyl glycinate groups, as a means for the controlled release of the steroid.[210] In a similar fashion, a controlled release system has been developed based on polyphosphazenes that bear amino acid ester side groups and covalently bound naproxen [(+)-2-(6-methoxy-2-naphthyl)propionic acid].[211]



3.84



3.85

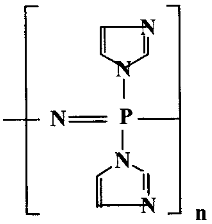
Schacht and coworkers in Belgium[201,212] used pellets of a polyphosphazene with both ethyl glycinate and ethyl phenylalanate side groups for the controlled release of the antitumor agent, mitomycin-C. A 100% ethyl glycinato polymer released the drug too rapidly, but mixed-substituent polymers with 50–65% phenylalanine ester released the drug at an optimum rate.

Laurencin and coworkers[213] have used a different approach to control the rate of bioerosion of polymers with amino acid ester side groups. They used hydrophobic 4-methylphenoxy cosubstituents (~50%) to slow the rate of hydrolysis, and these polymers were employed to study the rate of release of inulin. Similar polymers are also being developed by the same investigators as tissue engineering substrates for bone regeneration.[214–218]

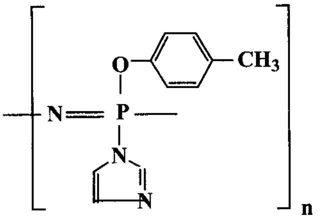
Veronese and coworkers in Italy used polymers with ethyl alanate side groups for the controlled release of anti-inflammatory agents, and for tissue regeneration in the treatment of periodontal disease. The same polymers have also been utilized in bioerodible nerve guide conduits for nerve regeneration.[219]

Table 3.2 lists some of the amino acid groups that have been studied as side groups for bioerodible phosphazenes, both as single-substituent and mixed-substituent species.

Amino acid ester side groups are not the only units that sensitize the system to hydrolysis. The *imidazolyl* group has an even greater effect.[197,198,219] For example, polymer **3.86**, prepared by the reaction of poly(dichlorophosphazene) with imidazole, is so unstable hydrolytically that it decomposes in moist air to imidazole, phosphate, and ammonia. This is too high a sensitivity for most biomedical applications. Hence, an emphasis has been placed on the study of polymers such as **3.87** in which a hydrophobic cosubstituent group, such as aryloxy, is present to reduce the rate of erosion.



3.86



3.87

Table 3.2 Amino Acid Ester Side Groups That Have Been Linked to Polyphosphazenes to Generate Hydrolytic Instability and Bioerosion

$NHCH_2COOMe$ (Glycinate)
$NHCH_2COOEt$
$NHCH_2COO$-*t*-Bu
$NHCH_2COOCH_2Ph$
NHCH(Me)COOMe (Alanate)
NHCH(Me)COOEt
NHCH(Me)COO-*t*-Bu
$NHCH(Me)COOCH_2Ph$
NHCH(CHMe)COOMe (Valinate)
NHCH(CHMe)COOEt
NHCH(CHMe-)COO-*t*-Bu
$NHCH(CHMe-)COOCH_2Ph$
$NHCH(CH_2CHMe_2)COOMe$ (Leucinate)
$NHCH(CH_2Ph)COOMe$ (Phenylalanate)
$NHCH(CH_2Ph)COOEt$
$NHCH(CH_2Ph)COO$-*t*-Bu
$NHCH(CH_2C_6H_4$-4-OH)COOEt (N-Tyrosinate)
O-4-$C_6H_4CH_2CH(NH_2)COOEt$ (O-Tyrosinate)

The aryloxy substituent serves a specific purpose. For drug release applications, it is normally preferred that the device should erode steadily *from the outside* only. Polymers such as **3.86** are so hydrophilic that water absorption followed by catastrophic breakdown of the capsule may occur, with the result that the drug is released precipitously in a massive dose. This is a situation to be avoided. The hydrophobic groups in **3.87** prevent rapid water penetration and, in so doing, limit the hydrolysis to the surface layers.

Polymer **3.87** has been evaluated as a matrix for the controlled release of progesterone.[197] It was first shown that the rate of release of this steroid and of bovine serum albumen can be controlled by variations in the ratio of aryloxy to imidazolyl side groups atached to the polyphosphazene chain. In vitro and in vivo studies were conducted to examine the release rate of labelled steroid from devices implanted subcutaneously in rats. Typical data are shown in Figure 3.22. The biocompatibility of this system, at least in rats, was found to be good.

Water-Soluble, Bioactive Polymers

In principle, water-soluble macromolecular drugs may be more effective than their small-molecule counterparts because of their restricted ability to diffuse to nearby tissues. For example, solutions of a polymeric drug would be injected into a compartment of the body or into a tumor, and the diffusion of the carrier polymer from that site would be restricted by the inability of polymer molecules to pass through semipermeable membranes. Targeting groups can also be linked to the macromolecule to further increase the effectiveness of the drug. The macromolecular component of such drug–polymer conjugates should be biodegradable in order to prevent the eventual deposition of the polymer molecules at some site in the body, for example in the spleen. The release of the small-molecule drug may precede, parallel, or follow hydrolytic

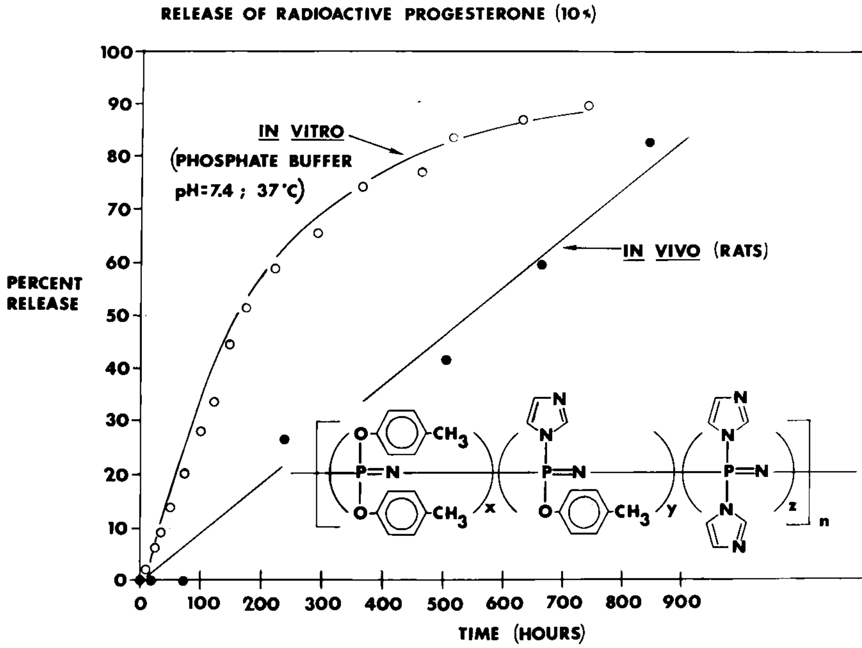


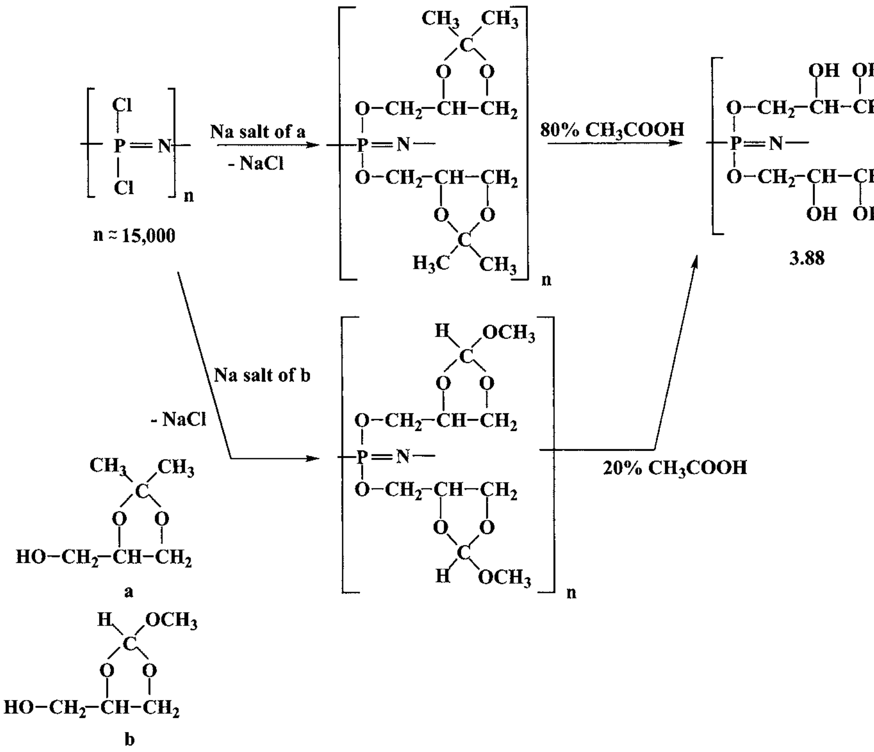
Figure 3.22 Release rate of radioactive progesterone from an erodable matrix of a poly(imidazolyl-aryloxy)phosphazene polymer. From Laurencin, Koh, Neenan, Allcock, and Langer, reference 197.

breakdown of the polymer skeleton. Thus, the three key components of molecular design are: (a) use of a bioerodible polymer, (b) the choice of water-solubilizing side groups, and (c) selection of a hydrolyzable linkage between the drug and the polymer.

Water solubility for phosphazene polymers can be achieved through the use of side groups such as methylamino, alkyl ether, glucosyl, or glyceryl side groups. Only the last two also favor hydrolytic instability. The glyceryl- and glucosyl-substituted polymers offer many potential advantages and some challenges as well. The glyceryl species are described here as an example.

Glyceryl-substituted polyphosphazenes are both water-soluble and slowly hydrolyzed in water. However, the synthesis of these polymers required a special approach. Glycerol is a trifunctional reagent. Attempts to use such glycerol as a nucleophile for reaction with poly(dichlorophosphazene) would lead to cross-linking of the system. Hence, the linkage of glycerol to the polymer chain must be preceded by protection of two of the hydroxyl groups. After the macromolecular substitution reaction has been carried out, the protected groups must be deprotected. The chemistry is outlined in reaction (58).[206]

Poly[*bis*(glyceryl)phosphazene] (**3.88**) is soluble in water, and it is hydrolyzed slowly to glycerol, which can be metabolized readily, and to phosphate and ammonia. A further advantage of this polymer is that the pendent hydroxyl groups are sites for the attachment of drug molecules. If a water-insoluble derivative is needed, this can be accomplished by the use of hydrophobic cosubstituents or by cross-linking of the chains.

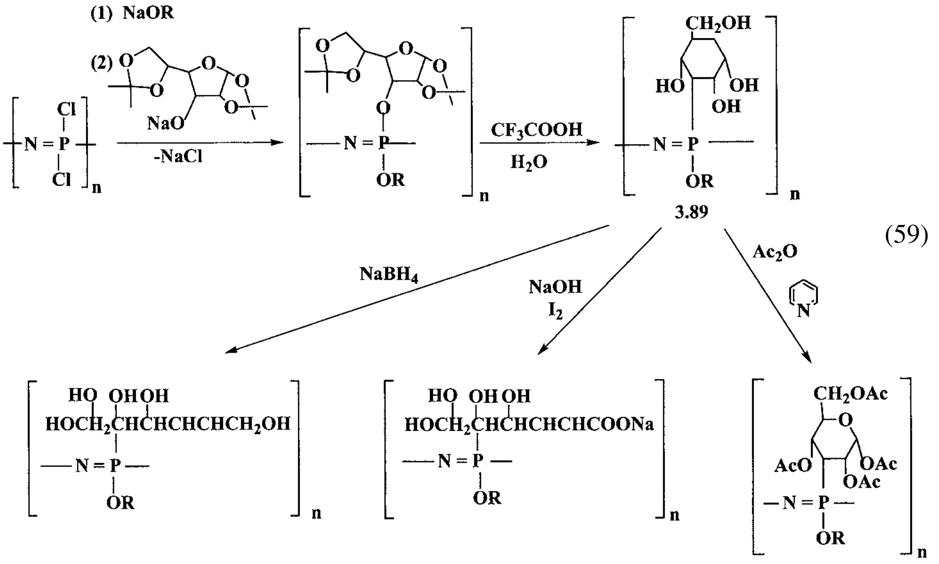


(58)

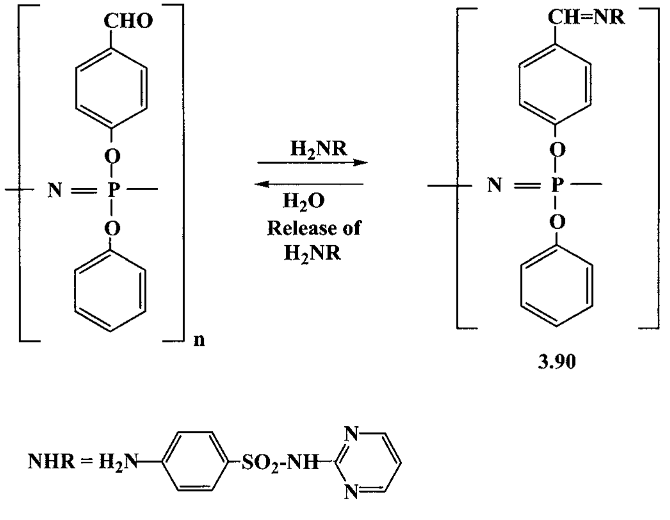
Polyphosphazenes that bear glucosyl side groups (**3.89**) are also promising bioerodible biomedical polymers.[205] They are prepared by the pathway shown in reaction sequence (59). Moreover, the synthesis of polymers with varying ratios of glucosyl to other side groups allows the system to be fine tuned with respect to water-solubility, surface character, and hydrolytic stability or instability. In some respects, glucosyl polyphosphazenes can be viewed as "inorganic polysaccharides," with close similarities being evident to an amorphous cellulose, and with all the side-group reactions that are available for cellulose.

Linkage of drug molecules to a water-soluble polyphosphazenes through a hydrolytically-labile linkage can be accomplished in several different ways. An example approach is shown by structure **3.90**, prepared via reaction (60).[220] An aldehydic group at the terminus of an aryloxy side unit is allowed to form a Schiff's base linkage to a biologically active amine. Schiff's base linkages are hydrolytically unstable. Hence, exposure to water cleaves this bond and brings about release of the bioactive agent. Amino-4-picoline, sulfadiazine, and dopamine have been immobilized and released from polyphosphazenes by this mechanism.[220] As in the previous example, the rate of release can be controlled by the ratio of phenoxy to substituted phenoxy units in the polymer.

A related approach is to synthesize a polyphosphazene with an amino-drug linked directly to phosphorus through a side-group phosphorus-nitrogen bond. The procaine derivative shown in **3.91** is a typical example designed to release the local anesthetic as an adjunct to dental or minor surgical procedures. Derivatives that contain benzocaine,



(59)

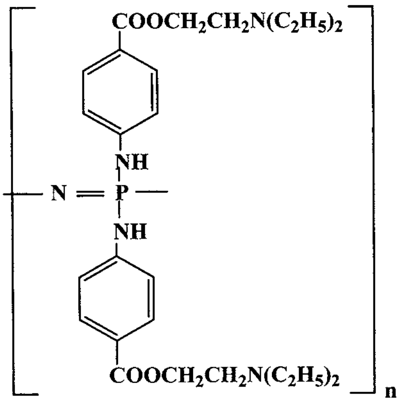


(60)

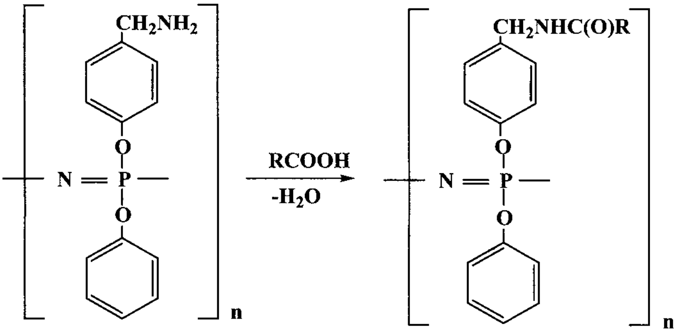
chloroprocaine, butyl *p*-aminobenzoate, and 2-aminopicoline side-group residues have also been prepared.[221]

The amido linkage is relatively labile in an aqueous environment. Hence, it is a promising connector group to link bioactive molecules with carboxylic acid units to polyphosphazenes that have amino groups in the side chain structure. An example is shown in reaction (61) as **3.92**. By this means, oligopeptides, *N*-acetyl-DL-penicillamine, *p*-(dipropylsulfamoyl)benzoic acid, and nicotinic acids can be linked to a polyphosphazene structure.[222] Such species can be water-insoluble but bioerodible, or water-soluble, depending on the cosubstituent groups.

Some drugs can also be linked to a water-soluble polymer by coordination. The platinum complex, $(NH_3)_2PtCl_2$, is a well-known antitumor agent. Because the drug is

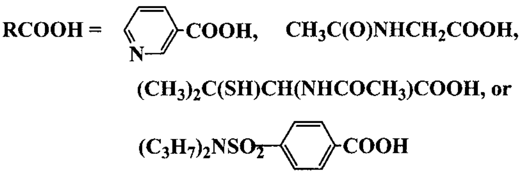


3.91



3.92

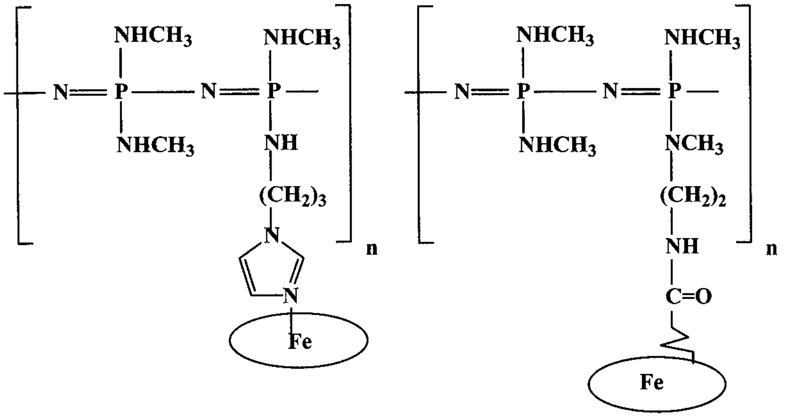
(61)



soluble in water, it is readily excreted through the kidneys and can cause severe kidney damage. Various procedures are employed clinically to minimize these side effects, but the linkage of the $PtCl_2$ component to a non-excretable, water-soluble polymer offers an additional possibility for improving the effectiveness of the chemotherapy.[223-225] As discussed earlier, a water-soluble polyphosphazene that is itself a base, and which can replace the ammonia ligands in $(NH_3)_2PtCl_2$, has been studied as a carrier macromolecule. The polymer is poly[*bis*(methylamino)phosphazene], $[NP(NHCH_3)_2]_n$. It forms a coordination complex with $PtCl_2$. Coordination involves the backbone nitrogen atoms rather than the methylamino side groups. Preliminary tissue culture testing has been carried out using this polymer, and it appears that some of the antitumor activity is retained in the polymeric drug. This result is interesting and perhaps surprising since the active form of $(NH_3)_2PtCl_2$ is believed to be the small-molecule diaquo derivative, $(H_2O)_2PtCl_2$, which must penetrate the tumor cell membrane in order to affect DNA replication.

Thus, more work is needed to understand the behavior of macromolecular drugs of this type, and the role played by dissociation or endocytosis (engulfment of the polymer by the cell) in their biological activity.

In another area, water-soluble polyphosphazenes have been studied as carrier macromolecules for heme and other iron porphyrins (**3.93** and **3.94**).[226,227] (In these structures the elipse and Fe symbol represent heme, hemin, or a synthetic heme analogue.)



3.93 3.94

Microspheres, Vesicles, and Micelles for Drug Delivery

A final biomedical use for polyphosphazenes is as components in microspheres, vesicles, and micelles for use in drug-delivery applications. Microspheres are pseudo-spherical constructs that range in size from 1 to 600 microns. Vesicles (lipozomes) are hollow, water-filled bilayer spheres with diameters that range from 0.03 to10 microns. Micelles typically have diameters near 1 micron (100 nanometers). Idealized representations of these three structures are shown in Figure 3.23, together with the location of trapped drug molecules.

Microspheres prepared from bioerodible polymers may be used for controlled drug delivery, cardiovascular imaging, or for microencapsulation of living cells. The polyphosphazene, $[NP(OC_6H_4COOH)_2]_n$, (known as PCPP, "Poly(carboxyPhenoxyPhosphazene)") has proved to be particularly useful for microsphere preparation.[228–235] It is prepared from $[NP(OC_6H_4COOR)_2]_n$ (where R = Et or Pr) by hydrolytic deprotection of the ester groups. The free acid polymer is insoluble in water or aqueous acid, but is soluble in aqueous base or, as its sodium salt, in water. However, the sodium salt form becomes insoluble when brought into contact with di- or tri-valent cations such as Ca^{2+} or Al^{3+} because of the formation of ionic cross-links (Figure 3.24). In practice, the cross-linking process converts the water-soluble polymer to a hydrogel or a tightly cross-linked solid depending on the amount of calcium in the system. The cross-linking can be reversed when the system is infused with a monovalent cation such as Na^+ or K^+. This property opens pathways for the entrapment of drug molecules or vaccines in the microsphere and release of them by changes in pH or cation concentrations.

Microspheres are prepared either by spraying a solution of the polymer plus the bioactive species into an aqueous solution of calcium chloride or by coascervation.[233]

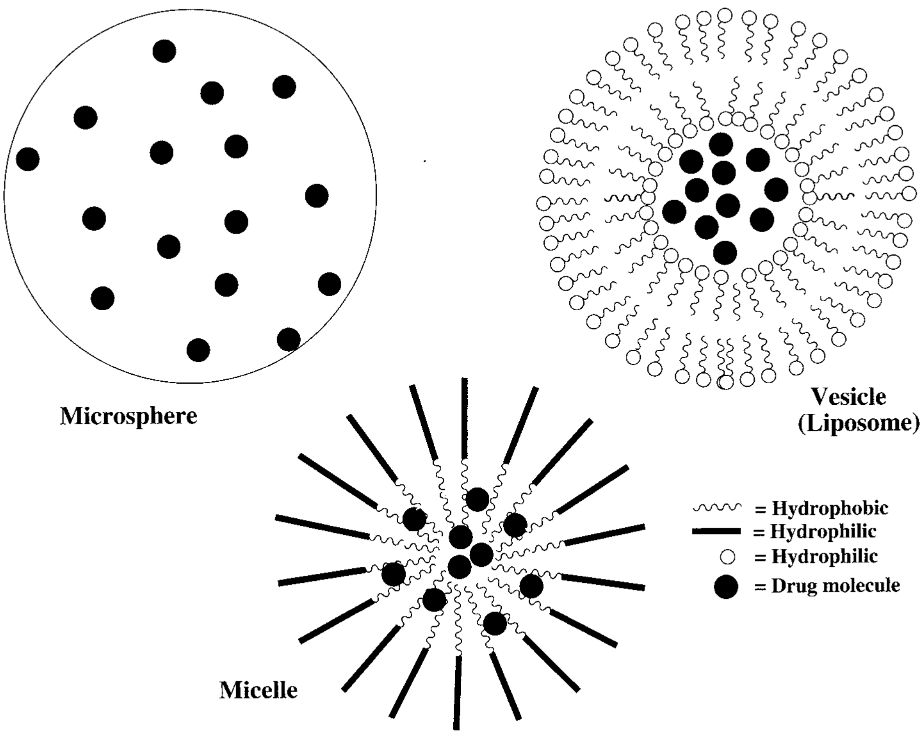


Figure 3.23 Representations of the different structures of microspheres, vesicles, and micelles. Polyphosphazenes are being developed for all three systems.

Coascervation involves first a precipitation of the sodium salt of PCPP plus the bioactive agent from water using the common ion effect through the addition of a solution of a sodium salt. This precipitates microspheres as a colloid, with each particle containing trapped bioactive units. Addition of the colloid to an aqueous solution of a calcium salt then causes cross-linking within the microspheres via the calcium ions. This approach gives smaller microspheres and with a more uniform diameter. When administered orally to a patient, the microspheres protect the bioactive agent from the acidity within the stomach, but release it as the polymer undergoes ionic decross-linking via sodium ion present in the small intestine. These microspheres have been used for the protection of hybridoma liver cells for possible use in artificial organs, and have been developed extensively as an oral delivery vehicle for influenza vaccines.[231–235] In this application, the polymer also serves as an adjuvant to enhance the activity of the vaccine. The vaccine delivery system has reached the stage of human clinical trials.

In a related development, the water-soluble polyphosphazenes, $[NP(OCH_2CH_2NMe_2)_2]_n$ and $[NP(NHCH_2CH_2NMe_2)_2]_n$ form 80 nm particles (polyplexes) when complexed to plasmid DNA. These particles may be used for gene delivery experiments.[236]

Vesicles are usually derived from hydrophobic oligomeric chains that are terminated by a hydrophilic end group. Fatty acids are the prototypical molecules that form double

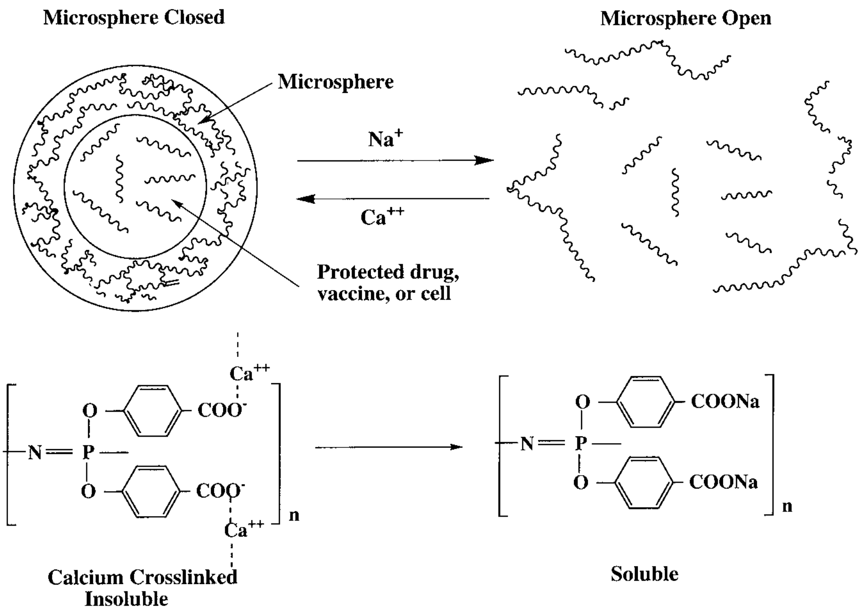
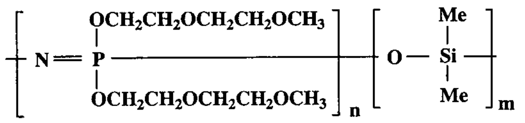


Figure 3.24 Microspheres produced from a calcium ion cross-linked polyphosphazene, illustrating the way in which these are used for the controlled delivery of vaccines.

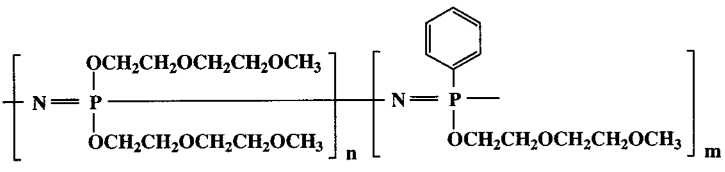
layer vesicles. The central cavity of a vesicle can be used as a reservoir for drug molecules, which are released when the vesicle disintegrates. Few vesicular systems have yet been reported for phosphazenes, but they should be readily available through the living cationic polymerization technique.

However, polyphosphazene micelles are known. These are formed by sonication of aqueous suspensions of amphiphilic diblock copolymers—macromolecules in which one block is hydrophilic and the other is hydrophobic. Both blocks may be phosphazene-based, or one block can be a phosphazene and the other an organic polymer. Polymers of this type are assembled via the living cationic polymerization discussed earlier. The polymers shown as **3.95–3.99** illustrate the range of structures that have been studied and the size of the micelles formed.[237–240]



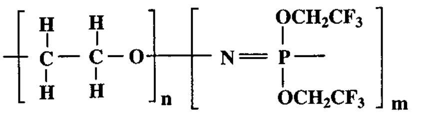
No micelles,

3.95



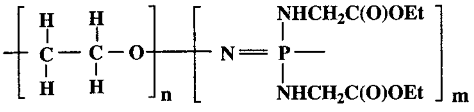
120 nm micelle

3.96



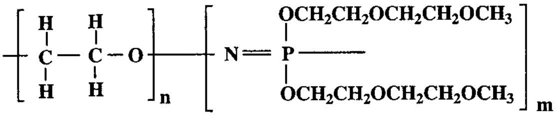
3.97

100-120 nm micelles



3.98

120-130 nm micelles



3.99

Possible micelles above 65°C
Hydrogel changes near 55°C

3.12 Optical and Photonic Polymers

3.12.1 Purpose

In polyphosphazene chemistry, the side groups usually define many of the properties. Nowhere is this more true than for those polymers which bear large, rigid aryl side groups. There are three potential uses for such polymers—as liquid-crystalline materials, as non-linear optical polymers, and as controlled, high refractive index glasses. Such side groups have a tendency to stack or undergo alignment in the solid state or even in the molten state to generate crystallinity or liquid crystallinity. When two or more different side groups of this type are present, the tendency to generate order may be reduced, but the large number of pi electrons in the side groups will generate a high refractive index. Such polymeric glasses are of interest for their possible uses in lenses, optical waveguides and perhaps eventually, as connectors for non-linear optical devices in optical integrated circuits. A potential advantage of polyphosphazenes in opto-electronic applications is that all three types of side groups can be linked to the same polymer chain.

3.12.2 Liquid-Crystalline Polyphosphazenes

First, we will consider the design of polyphosphazenes as side-chain liquid-crystalline materials.[241–248] Side-chain liquid-crystalline polymers are a subclass of species described earlier as structure **3.72**. Liquid crystallinity occurs when the rigid side groups become organized, usually in the semi-liquid state. The organization may be nematic (oriented but unlayered) or smectic (layered) as illustrated in Figure 3.25.

The essential components of such a systems are: (1) A highly flexible polymer chain that responds to the alignment needs of the rigid "mesogenic" units rather than

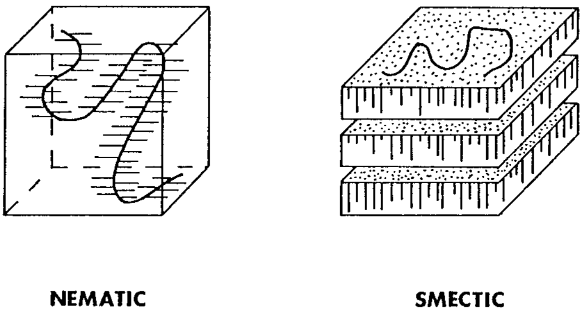
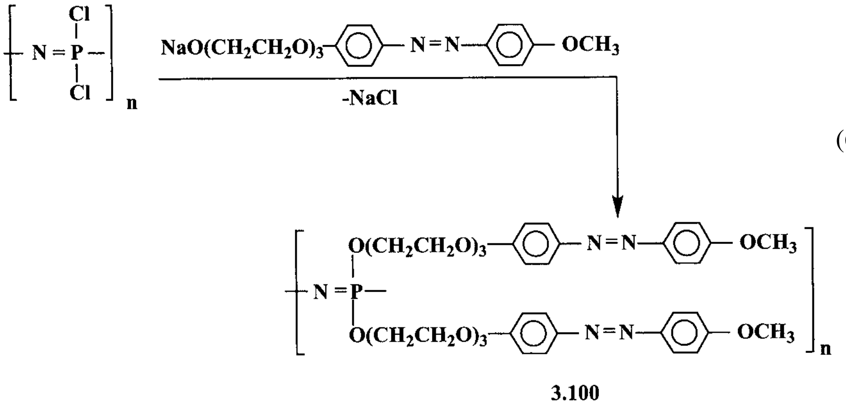


Figure 3.25 Side-chain liquid crystallinity occurs when rigid side groups (mesogens) can form arrays or stacks. The appearance of this phenomenon requires a flexible main chain (such as a polyphosphazene or polysiloxane chain) and a flexible spacer unit that links the main chain to the mesogen and decouples the motions of the main chain from those of the mesogens.

dictating the orientation of side groups. Polyphosphazene chains have this flexibility. (2) A flexible spacer group that decouples the thermal motions of the chain from the alignment of the mesogens. Oligoethyleneoxy spacer groups often serve this purpose. And (3) the mesogen itself—biphenyl units, for instance, or aromatic azo groups.

The synthesis of one example of a liquid-crystalline polyphosphazene is shown in reaction (62).[241–248] This orange-yellow polymer (**3.100**) changes from a glassy microcrystalline material to the rubbery microcrystalline state at the glass transition (T_g) at 79 °C. Further heating raises the temperature to the microcrystallite melting transition (T_m) at 118 °C. But even in the molten state the polymer retains some order, as indicated by the pattern seen through a microscope fitted with crossed polarizers (Figure 3.26). The texture of the pattern is indicative of a nematic-type liquid-crystalline system. The birefringence obtained from the analogous cyclic trimer is also shown in Figure 3.26. Further heating of this polymer to 126 °C breaks the liquid-crystalline order, and the material now behaves as an isotropic liquid, showing only a dark field when viewed between crossed polarizers.



(62)

3.100

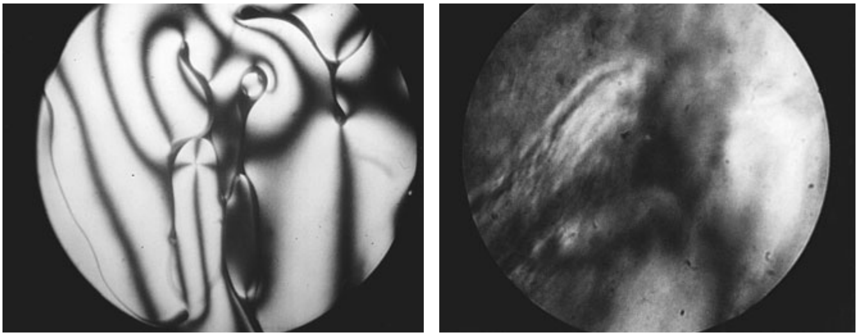


Figure 3.26 Photographs taken through a polarizing microscope of (left) a cyclic trimeric phosphazene bearing six p-CH3OC6H4N=NC6H4(OCH2CH2)2O- side-group units, and (right) a related high polymer, with the samples heated above the normal melting point of 111–112 °C for (left), and 118 °C for (right).

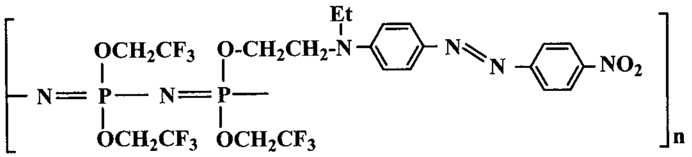
Other similar polymers with both aromatic azo mesogenic groups and "inert" cosubstituent groups (OCH_2CF_3) have also been found to form a liquid crystalline phase. It seems clear that a wide range of related derivatives will behave similarly. However, the length of the spacer group between the mesogen and the chain is critical. If the spacer group in compound **3.100** is shortened to only one ethyleneoxy unit, the liquid-crystalline behavior disappears. The terminal group on the mesogen also has a strong influence on liquid crystallinity.

Cyclic trimeric and tetrameric phosphazenes with mesogenic side groups also generate liquid-crystalline systems.[245,249]

3.12.3 Non-Linear Optical Materials

Another important class of opto-electronic materials are those that undergo a change in refractive index or bring about a doubling or tripling of the frequency of light passing through them following the application of an electric field. Such "non-linear" materials are of interest for uses in optical switches and other components in optical communications technology. Chemical units that exhibit this behavior include conjugated unsaturated organic molecules such as aromatic azo or cinnamyl groups. However, small molecules with these structures must crystallize in a non-centrosymmetric crystalline lattice before non-linear optical effects can be detected, and this is quite rare. However, when such units are present as side groups linked to a polymer chain, it is possible to align them through an external force in order to generate a non-symmetric orientation.

For example, the polyphosphazene shown as **3.101** can be solution-cast to give thin films.[250–254] When the films are heated above the T_g and are subjected to a kilovolt-level electric field, the polarizable, conjugated aromatic side chains become oriented in the direction of the field. This orientation is partly frozen in place by rapid cooling. Such a film will double the frequency of a laser beam that passes through it (while halving the intensity) as long as the side-group orientation is retained. Immediately after poling, the effect is almost as large as seen in inorganic NLO crystals such as lithium niobate,



3.101

but the effect is lost rapidly as the side groups lose their orientation due to thermal motion. Polyphosphazenes with higher T_gs would retain the phenomenon for longer period of time.

Some debate is evident about the role of the phosphazene polymer backbone in the generation of third-order NLO activity.[255,256]

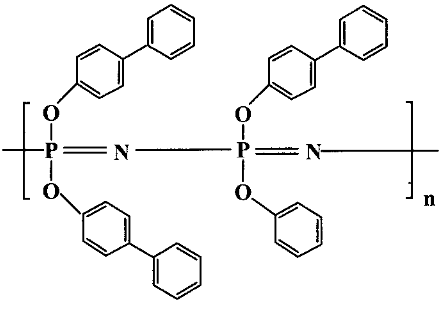
3.12.4 Controlled Refractive Index Polymers

A need exists for glassy, transparent polymers that have easily controlled refractive indexes, and especially those that have high refractive indexes coupled with low optical dispersion. Such materials are needed for lightweight, easily fabricated lenses and prisms, and also for possible uses in lightweight optical waveguides or optical switches. Polymers that undergo a large refractive index change as the temperature is raised are of interest for thermally activated optical switches. Polyphosphazenes with electron-rich side groups offer an attractive route to achieving these goals, and attention has been focused on side groups that contain multi-aromatic side units and/or halogen atoms in the side-group structure.

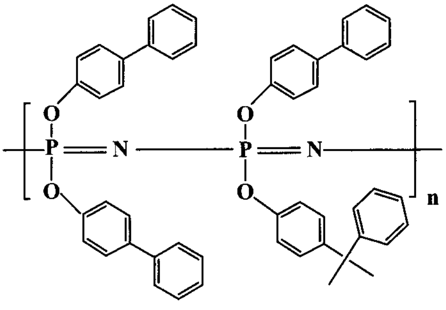
The introduction of bulky, electron-rich side groups, such as those depicted in structures **3.102–3.105** requires the use of special experimental conditions. If introduced via an aryloxide ion by the macromolecular substitutive route, these side groups impart and suffer considerable steric hindrance. Replacement of every chlorine atom along the phosphazene chain by organic side groups may be difficult.

Thus, forcing reaction conditions are usually needed, and these are provided by raising the temperature of the substitution reaction into the 120–150 °C range. Because solvents such as tetrahydrofuran (which boil near 70 °C) are normally used for these reactions, the substitution must be carried out in sealed, medium pressure reactors to prevent loss of the solvent. Using these reaction conditions, it has been possible to synthesize a broad range of polymers, including those shown in **3.102–3.105**.[257–261] Some of these polymers are microcrystalline. Others (usually those with two different side groups) are amorphous. All have high refractive indices because of the large number of pi-electrons in the side groups. Polymer **3.102** is an amorphous glass at temperatures up to 60 °C and has a refractive index of 1.65. Bromine or iodine atoms (**3.105**) add additional electron density, and raise the refractive indices to the level of 1.75, values that are among the highest known for polymers. The pi-bonds in the phosphorus-nitrogen backbone undoubtedly play a role in this effect.

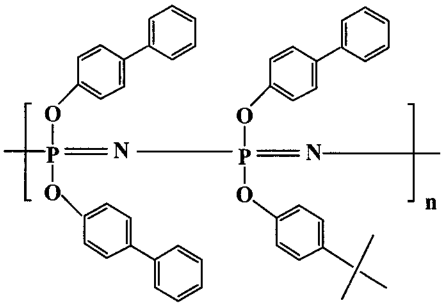
Some of the latest work on high refractive index polyphosphazenes makes use of polymers that contain both fluoroalkoxy and di- or tri-chlorophenoxy side groups.[261] These amorphous glasses are thermally stable up to 400 °C, show a large variation of refractive index with temperature, and refractive index values that vary from 1.39–1.56 depending on composition. Thus, they are candidates for uses in thermo-optical switching devices.



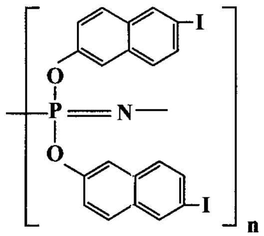
$T_g = 63°C$ η = 1.65
3.102



$T_g = 59°C$ η = 1.65
3.103



$T_g = 68°C$ η = 1.69
3.104



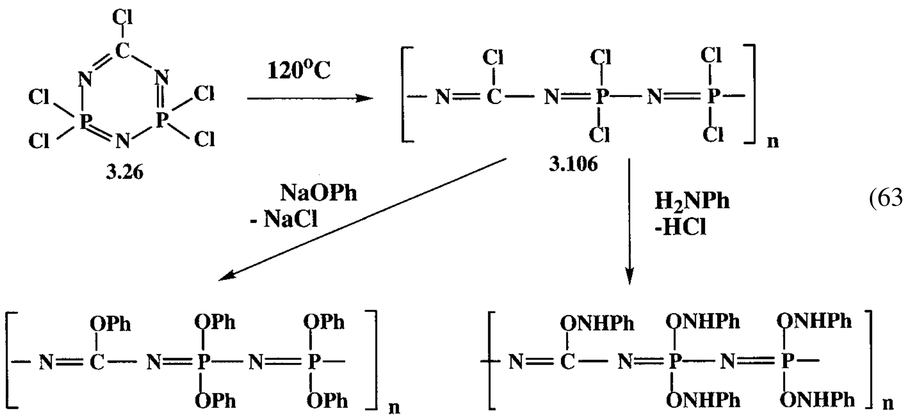
T_g 111 η = 1.75
3.105

3.13 Polymers Related to Polyphosphazenes

3.13.1 Poly(carbophosphazenes)

Long-chain polymers based on a skeleton of alternating phosphorus and nitrogen atoms may be considered as the "parent" systems for other macromolecules that contain phosphorus, nitrogen, and some other element in the skeletal system. The first examples of these new systems were the poly(carbophosphazenes) which contain phosphorus, nitrogen, and carbon in the backbone structure.[262,263] They are prepared by the polymerization of a chlorocarbophosphazene cyclic compound (**3.26**), followed by the thermal polymerization of this species to the high polymer **3.106**, and the subsequent replacement of the chlorine atoms in this macromolecule by organic side groups (reaction sequence (63)). An example of these polymers are shown in Table 3.1.

An interesting feature of these polymers is that, for a given side group, the glass transition temperature of the poly(carbophosphazene) is significantly higher than that of the corresponding classical polyphosphazene. This implies that the presence of the sketelal carbon atoms brings about a decrease in the flexibility of the backbone, probably because a C=N double bond has a higher barrier to torsion than a P=N bond. This occurs in spite of the fact that the carbon atoms bear only one side group instead of two, which would be expected to lower the overall intramolecular interactions between



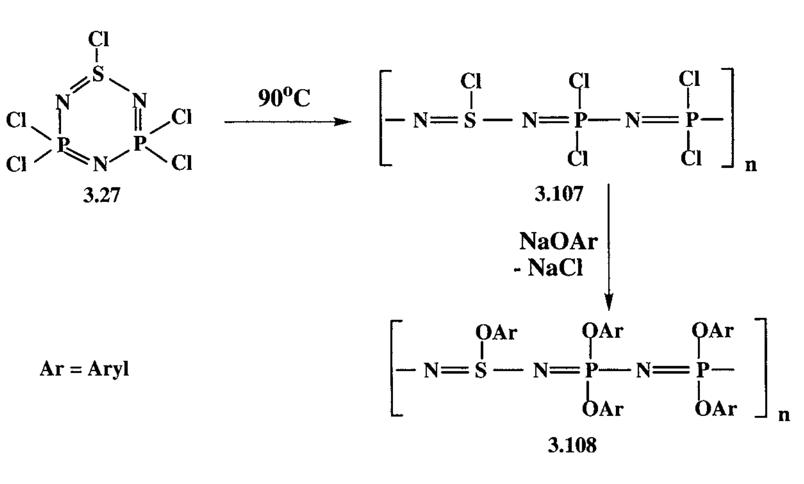
(63)

the organic side groups. The decreased flexibility associated with the C=N bonds may reflect the "organic" p_π-p_π double bond nature of these linkages in contrast to the d_π-p_π bonding in phosphazenes.

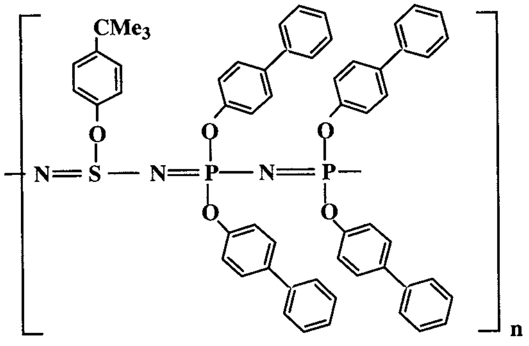
The poly(carbophosphazenes) that have been synthesized are amorphous rather than crystalline, and they appear to retain the same atom sequencing along the chain as in the cyclic trimer from which they are derived. Hence, repeating group scrambling during polymerization does not appear to be a significant component of the process.

3.13.2 Poly(thiophosphazenes)

The second group of new polymers contain sulfur atoms in the skeleton in addition to the normal phosphorus and nitrogen atoms.[264,265] They too are synthesized by the ring opening polymerization of a heterocyclic inorganic species (**3.27**), followed by macromolecular halogen replacement reactions carried out on the resultant polymer (**3.107**) (reaction (64)). The properties of the organo-substituted polymers (**3.108**) are different again from those of polycarbophosphazenes and classical polyphosphazenes,



(64)



3.109

For example, the glass-transition temperatures generally fall between those of classical polyphosphazenes and poly(carbophosphazenes) when the same side groups are present. Unlike both polyphosphazenes and poly(carbophosphazenes), some poly(thiophosphazenes) with organic side groups are sensitive to water. This is the case even when hydrophobic phenoxy side groups are present, and it is inferred that the relatiavely exposed sulfur IV atoms are the sites of hydrolytic attack. To overcome this sensitivity it is necessary to protect the skeleton by very bulky organic side groups such as 3-phenylphenoxy or 4-phenylphenoxy units, although this creates synthetic problems associated with the replacement of every chlorine atom in the macromolecular intermediate by the bulky aryloxy units. Compound **3.109** is stable to water, and has a T_g of 69 °C.

3.13.3 Poly(thionylphosphazenes)

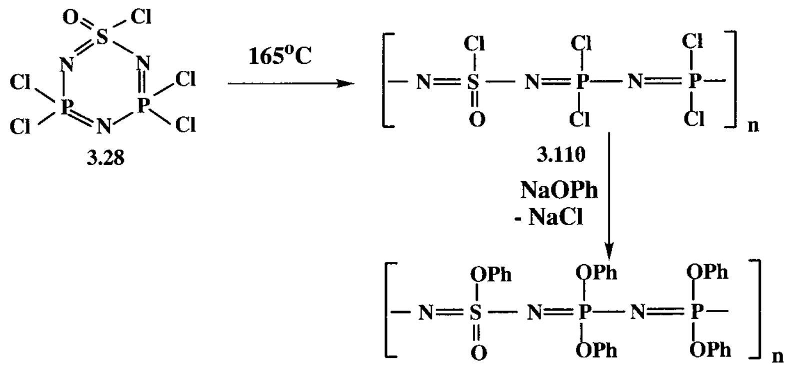
A third variant on the polyphosphazene skeletal structure is represented by the poly(thionylphosphazenes) (reactions (65) and (66)) in which every third phosphorus along the chain is replaced by a sulfur VI atom.[266–272] These species are more hydrolytically stable than their sulfur IV analogues, probably because the presence of two side groups on sulfur provides additional protection for the main chain.

Thermal polymerization of the appropriate cyclic trimer leads to the macromolecular intermediates shown in **3.110** and **3.111**. Subsequent halogen replacement by aryloxides or amines completes the process. The presence of chlorine or fluorine on the sulfur VI atoms allows scope for regiospecific substitution because these halogens are less reactive than their counterparts attached to the phosphorus atoms. Indeed, when aryloxy groups are linked to phosphorus, the halogen atoms on sulfur are stable to water. All the known polymers in this class are amorphous materials with glass transition temperatures that range from –25 °C to +82 °C, depending on the organic substituents.

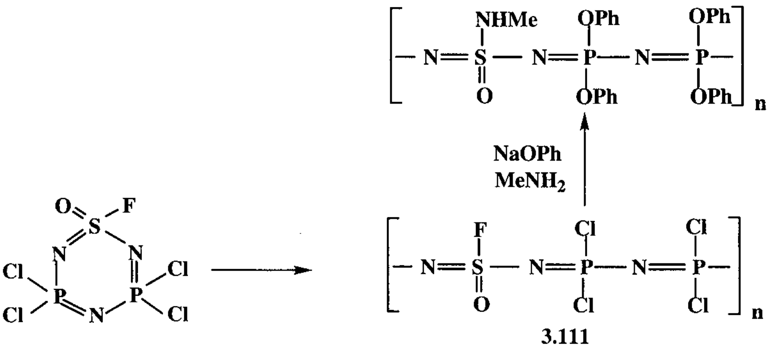
It seems likely that phosphazene polymers with carbon or sulfur in the backbone are the forerunners of many new polymer systems that will be investigated in the coming years.

3.14 Conclusions

The polyphosphazene systems comprise some of the most diverse macromolecules yet discovered. Because of space limitations, many aspects of polyphosphazene chemistry



(65)



(66)

have not been included in this survey. The reference list for this chapter covers less than one-tenth of the total number of publications and patents on this subject. The selection of topics for this chapter was made on the basis of fundamental chemistry, and many applied aspects have not been discussed. However, it will be clear that the fundamental chemistry has spawned a very broad range of potential technological developments. Many of these developments reflect the pivotal position occupied by polyphosphazene chemistry as a bridge between organic polymers and inorganic materials.

Compared to many areas of polymer chemistry the field of polyphosphazenes is quite new. The first stable poly(organophosphazenes) were synthesized only in the 1960s at a time when the conventional wisdom held that all the major polymer systems had already been discovered, and that polymers based on the inorganic elements were likely to be brittle, insoluble, intractable materials. The sequence of synthetic discoveries in this area, outlined in Figure 3.27, illustrates how the development of a new inorganic-based polymer system can occur.

In many respects, the polyphosphazenes are the prototype inorganic backbone polymers, that exemplify the principles of ring-opening and condensation polymerization, macromolecular substitution reactions and their potential for molecular design, and an enormous range of derivatives with the same backbone but different organic side groups.

In addition, the variety of different phosphazene polymer architectures and hybrid systems that are now appearing, including block, comb, and graft copolymers, star structures, cyclolinear polymers, and composite systems, generates a diversity of properties that equals and often exceeds the range found in most organic polymer systems. Yet they represent just one skeletal elemental combination—that of phosphorus and nitrogen. Literally scores of other inorganic skeletal systems can be visualized, each of which may give rise to an equally diverse polymer chemistry. These possibilities are illustrated further in the two chapters that follow, in which the emphasis is on inorganic macromolecules derived from the element silicon.

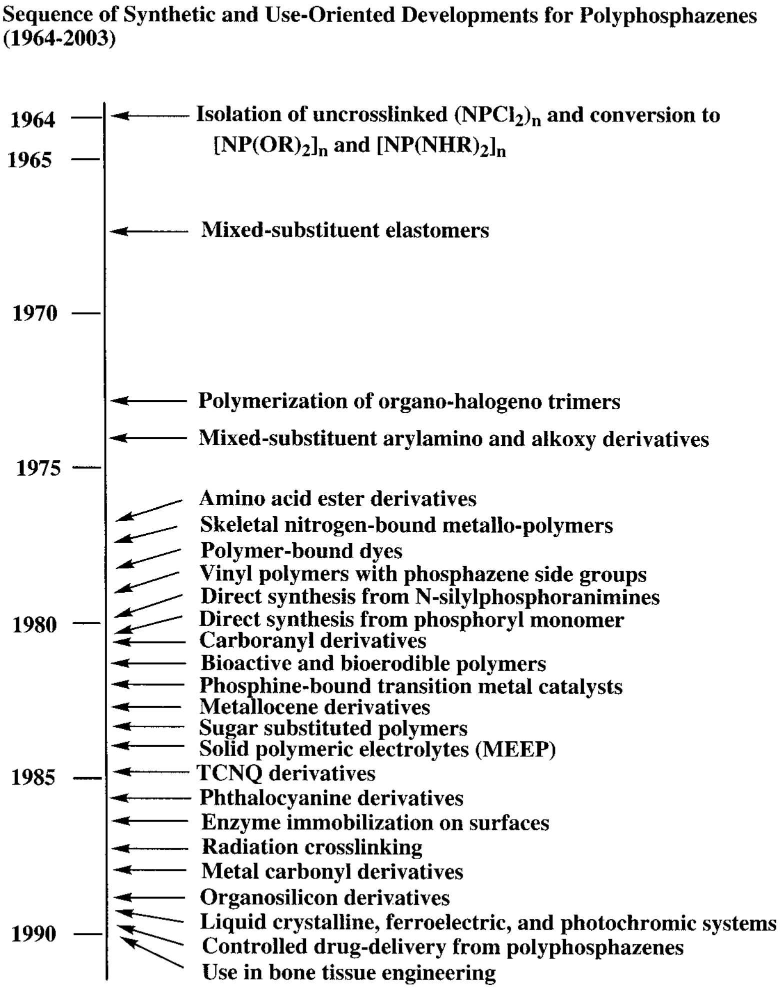


Figure 3.27 Approximate sequence of developments in the synthesis and uses of polyphosphazenes since 1964. (*continued on following page.*)

Sequence of Developments (continued)

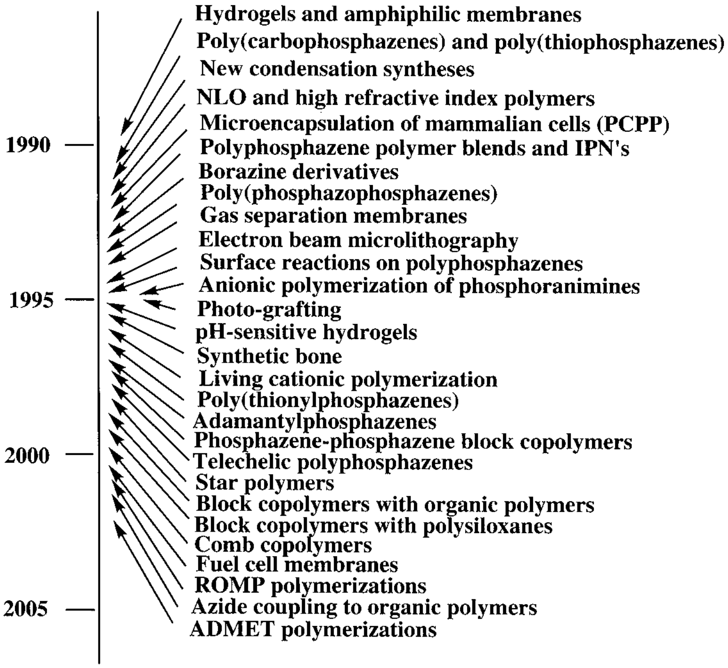


Figure 3.27—cont'd.

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4

Polysiloxanes and Related Polymers

4.1 Introduction

At the present time, polysiloxanes are unique among inorganic and semi-inorganic polymers. They have been the most studied by far, and are the most important with regard to commercial applications. Thus, it is not surprising that a large number of review articles exist describing the synthesis, properties, and applications of these materials.[1–55]

The Si-O backbone of this class of polymers endows it with a variety of intriguing properties. For example, the strength of this bond gives the siloxane polymers considerable thermal stability, which is very important for their use in high-temperature application (for example as heat-transfer agents and high-performance elastomers). The nature of the bonding and the chemical characteristics of typical side groups give the chains a very low surface free energy and, therefore, highly unusual and desirable surface properties. Not surprising, polysiloxanes are much used, for example, as mold-release agents, for waterproofing garments, and as biomedical materials.

Some unusual structural features of the chains give rise to physical properties that are also of considerable scientific interest. For example, the substituted Si atom and the unsubstituted O atom differ greatly in size, giving the chain a very irregular cross section. This influences the way the chains pack in the bulk, amorphous state, which, in turn, gives the chains very unusual equation-of-state properties (such as compressibilities). Also, the bond angles around the O atom are much larger than those around the Si, and this makes the planar all-*trans* form of the chain approximate a series of closed polygons. As a result, siloxane chains exhibit a number of interesting configurational characteristics. These structural features, and a number of properties and their associated applications, will be discussed in this chapter.

The major categories of homopolymers and copolymers to be discussed are[31] (i) linear siloxane polymers [-SiRR′O-] (with various alkyl and aryl R,R′ side groups),

(ii) sesquisiloxane polymers possibly having a ladder structure, (iii) siloxane-silarylene polymers [-$Si(CH_3)_2OSi(CH_3)_2(C_6H_4)_m$-] (where the skeletal phenylene units are either *meta* or *para*), (iv) silalkylene polymers [-$Si(CH_3)_2(CH_2)_m$-], and (v) random and block copolymers, and blends of some of the above. Topics of particular importance are the structure, flexibility, transition temperatures, permeability, and other physical properties. Applications include high-performance fluids, elastomers, and coatings, surface modifiers, gas-separation membranes, photoresists, soft contact lens, body implants, and controlled-release systems. Also of interest are the use of sol-gel techniques to convert silicon-containing materials to novel reinforcing fillers or to polymer-modified ceramics, and the use of pyrolyses to form high-performance fibers.

4.2 History

The first reaction of relevance in this area was the conversion of elemental silicon to silicon tetrachloride $SiCl_4$ and to trichlorosilane $SiHCl_3$. These purely inorganic substances were then converted into organometallic species such as $RSiX_3$, by allowing them to react with diethyl zinc and related compounds.[2,3,16,24,28]

The entire area of organosilicon chemistry blossomed with Kipping's preparation of such compounds by the more convenient Grignard process. These silanes turned out to be of paramount importance since they hydrolyzed readily to form compounds containing Si-O bonds, both linear and cyclic.[12,22,24,28] These new materials were first called silicoketones or "silicones" by analogy with ketones in the organic area. Structural studies, however, showed that they did not contain the Si=O double bond. Thus, the silicone name is a misnomer, but it has persisted, at least in casual usage. However, the terms siloxanes and polysiloxanes are preferred.

4.3 Nomenclature

In most of the literature, the terminology consists simply of specifying the side groups and then the backbone. For example, the polymer having the repeat unit [-$Si(CH_3)_2O$-] is called poly(dimethylsiloxane), and that having the repeat unit [-$Si(CH_3)(C_6H_5)O$-] is called poly(methylphenylsiloxane). Closely related polymers are the poly(silmethylenes) of repeat unit [-$SiRR'CH_2$-] and the poly(siloxane-silphenylenes) of repeat unit [-$SiRR'OSiRR'C_6H_4$-], in which the second oxygen atom in the doubled repeat unit is replaced by a phenylene group.

Because certain structures and structural segments appear over and over again in the siloxane area, however, several abbreviations are used in specialized areas of the literature.[24] The monofunctional unit $R_3SiO_{0.5}$ is designated "M," the difunctional unit R_2SiO "D," the trifunctional unit $RSiO_{1.5}$ "T," and the quadrifunctional SiO_2 "Q." For example, the dimer $(CH_3)_3SiOSi(CH_3)_3$ is termed "MM," the oligomer $(CH_3)_3Si[OSi(CH_3)_2]_{10}OSi(CH_3)_3$ is termed "$MD_{10}M$," and the cyclic trimer $[Si(CH_3)_2O]_3$ is called "D_3." Unprimed abbreviations are taken to mean the R substituents are methyl groups, since these are the most common and the most important. Primed abbreviations are used for other substituents, the most important of which is probably the phenyl group.

4.4 Preparation and Analysis

4.4.1 Preparation of Monomers

The elemental silicon on which the entire technology is based is typically obtained by reduction of the mineral silica with carbon at high temperatures:[16,24]

$$SiO_2 + 2C \rightarrow Si + 2CO \tag{1}$$

The silicon is then converted directly to tetrachlorosilane by the reaction

$$Si + 2Cl_2 \rightarrow SiCl_4 \tag{2}$$

As already mentioned, this can be used to form an organosilane by the Grignard reaction

$$SiCl_4 + 2RMgX \rightarrow R_2SiCl_2 + 2MgClX \tag{3}$$

This relatively complicated reaction has been replaced by the so-called "Direct Process" or "Rochow Process,"[12,16,22] which starts from elemental silicon. It is illustrated by the reaction

$$Si + 2RCl \rightarrow R_2SiCl_2 \tag{4}$$

but the process also yields $RSiCl_3$ and R_3SiCl, which can be removed by distillation. Compounds of formula R_2SiCl_2 are extremely important, because they provide access to the preparation of a wide variety of substances having both organic and inorganic character.[56–59] Their hydrolysis gives dihydroxy structures which condense to give the basic [-SiR_2O-] repeat unit. The nature of the product obtained depends greatly on the reaction conditions.[59] Basic catalysts and higher temperatures favor higher molecular weight polymers that are linear. Acidic catalysts tend to produce cyclic small molecules or low molecular weight polymers.

The hydrolysis approach to polysiloxane synthesis has now been largely replaced by ring-opening polymerizations[16,28,59–64] of organosilicon cyclic trimers and tetramers, with the use of ionic initiation. These cyclic monomers are produced by the hydrolysis of dimethyldichlorosilane. Under the right conditions, at least 50 wt % of the products are cyclic oligomers. The desired cyclic species are separated from the mixture for use in ring-opening polymerizations such as those described below.

4.4.2 Ring-Opening Polymerizations

Cyclic siloxanes can undergo a ring-opening polymerization that is a chain-growth process. Free radicals are not useful as initiator species, because of the nature of the siloxane bond, but anionic and cationic initiators are very effective. The reaction is illustrated using the most common cyclic oligomers, the trimer hexamethylcyclotrisiloxane

or the tetramer octamethylcyclotetrasiloxane:[60,61]

$$\left(SiR_2O\right)_{3,4} \rightarrow \left[\text{-}SiR_2O\text{ -}\right]_x \quad (5)$$

where R can be alkyl or aryl and x is the degree of polymerization. In principle the reaction is reversible, but in practice it is made essentially irreversible by the choice of monomer, initiator, and polymerization conditions. Because of this potential reversibility, however, it is important to remove all initiators from the finished product, and this is typically done by neutralization of the acidic or basic terminal chain residues. Alternatively, some initiators can be removed by volatilization or thermolysis. Frequently, end blocking is used to modify the ends of the chains by placing groups there that will increase thermal stability and prevent re-equilibration.

Because it is frequently impossible to remove all traces of active species, some reorganization is almost inevitable. In these processes, siloxane bonds interchange so as to bring about variation in both molecular weight and in the relative amounts of cyclic and linear species. At equilibrium, a Gaussian distribution of molecular weights exists. The cyclic oligomers that occur most frequently are D_4 through D_6, and the amount obtained depends greatly on the "monomer" and on the polymerization conditions. They are typically present to the extent of 10–15 wt %. The lower molecular weight products are generally removed from the polymer before it is used in a commercial application. Their presence is also of interest from a fundamental scientific point of view, in two respects. First, the extent to which they are formed can be used as a measure of chain flexibility.[65–67] Second, the various cyclic species formed can be purified using standard separation techniques, and then used to test theoretical predictions of the differences between otherwise identical cyclic and linear molecules.[39,54,68–71]

For anionic equilibrations, typical catalysts are alkali metal oxides and hydroxides, and bases in general. Initiation and propagation involve nucleophilic attack on the monomer, causing opening of the ring followed by chain extension. As is frequently the case in ionic polymerizations, the nature of the countercation, particularly its size, can have a large effect on the reaction. This polymerization is very different from most others,[59] which are energetically driven, by a decrease in enthalpy. The decrease in entropy that accompanies the linkage of monomers into a chain-like structure is counteracted and overcome by the decrease in energy generated by the formation of new chemical bonds. In the siloxane case, the bonds linking the monomer units into the chain are similar in energy to those found in siloxane rings, and the net energy change is very small. However, there is an increase in entropy, presumably from increased internal molecular freedom of the siloxane segments in going from the cyclic structures to the linear chains. It is this increase in entropy that drives the polymerization reaction.

Cationically catalyzed polymerizations[28,72] have not received as much attention as the anionic variety. Typical cationic (acidic) catalysts in this case are Lewis acids. Yields and proportions of the various species are generally very similar to those obtained in anionic polymerizations, although the mechanism is very different. The reaction is thought to proceed through a tertiary oxonium ion formed by addition of a proton to one of the O atoms of the cyclic siloxane. Part of the mechanism may involve step growth, as well as the expected chain growth.

Polymerization of non-symmetrical cyclic siloxanes gives stereochemically variable polymers [-SiRR′O-] that are analogous to the totally organic vinyl and vinylidene

polymers [-CRR′CH_2-]. In principle, it should be possible to prepare them in the same stereoregular forms (isotactic and syndiotactic) that have been achieved for some of their organic counterparts,[8,59] as mentioned in Chapter 2. This has been accomplished now to some extent, as will be described below. The major advantage is the crystallizability generally observed for isotactic and syndiotactic stereoregular forms of a polymer, whereas the stereoirregular (atactic) modification is inherently non-crystallizable.

In some cases, an end blocker such as YR′SiR_2OSiR_2R′Y is used to form reactive -$OSiR_2$R′Y chain ends.[73,74] Some of the uses of these materials are described below.

Homopolymerizations of this type are discussed in detail elsewhere.[59,61]

4.4.3 Copolymerization

Polymerization of mixtures of monomers, such as $(SiR_2O)_m$ with $(SiR'_2O)_m$, can be used to obtain random copolymers. They are generally highly irregular in structure, but in a chemical rather than stereochemical sense. Correspondingly, they also show little if any crystallizability.

Copolymerizations of this type are also discussed in detail elsewhere.[59,61]

4.4.4 Structural Features

Several structural features make the siloxane backbone one of the most flexible in all of polymer science.[34,75,76] The reasons for this extraordinary flexibility can be seen from Figure 4.1. First, because of the nature of the bonding,[29,65–67,77] the Si-O skeletal bond has a length (1.64 Å) which is significantly larger than that (1.53 Å) of the C-C bond of paramount importance in most organic polymers. As a result, steric interferences or intramolecular congestion are diminished.[65–67] (This circumstance is true for inorganic and semi-inorganic polymers in general. Almost any single bond between a pair of inorganic atoms [Si-Si, S-C, Si-N, P-N, etc.] is longer than the C-C bond). Also, the oxygen skeletal atoms are unencumbered by side groups and they are as small as an atom can be and still have the di-valency needed to continue a chain structure. Also, the Si-O-Si bond angle ($180 - \theta'$) of ~143° is much more open than the usual tetrahedral bonding (occurring at ~110°), and can "invert"[78] through the linear (180° form) with little cost in energy. Similarly, torsional rotations can occur without serious increases in energy. These structural features have the effect of increasing the *dynamic* flexibility of

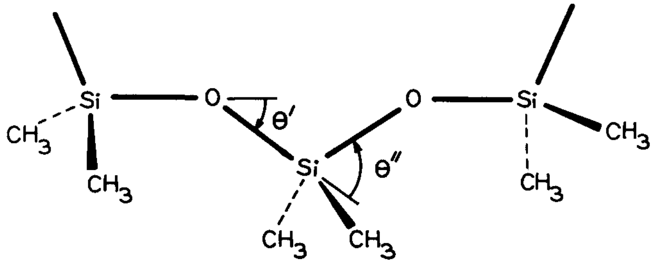


Figure 4.1 Sketch of the PDMS chain, showing some structural information relevant to its high flexibility.[65] Reproduced by permission of John Wiley and Sons.

the chain.[65–67] They also increase its *equilibrium* flexibility, which is the ability of a chain to take on a compact shape when in the form of a random coil. (It is generally measured, inversely, by the mean-square end-to-end distance or radius of gyration of the chain in the absence of excluded-volume effects.)

4.4.5 Elastomer Technology

Pure siloxane polymers are only rarely appropriate for use in technology. Numerous additives must generally be incorporated in order to improve their properties. A typical formulation contains the siloxane polymer, plus some or all of the following ingredients: reinforcing fillers, extending (non-reinforcing) fillers, processing aids, heat-aging additives, pigments, and curing agents (for example, end-linking agents with associated catalysts, or organic peroxides).[5,79]

The siloxane polymer usually has a rather high molecular weight, and may have reactive ends for end-linking curing or vinyl side chains for peroxide curing.

The preferred reinforcing filler is high surface area silica, particularly that made by the fume process.[80] This gives the greatest reinforcement, and because of its high purity, yields excellent electrical insulation properties. Silicas obtained from aqueous solutions impart only moderately good reinforcement and, because of the presence of water on the filler particles, can adversely affect the electrical properties of the elastomer. Carbon black provides some reinforcement, but can interfere with some types of peroxide cures. Also, its electrical conductivity can severely compromise the electrical properties of the material.[5,79] In some cases, silane coupling agents are used to improve the bonding between the reinforcing phase and the polymer.[81] These molecules typically have the structure X_3SiY, with X chosen to interact strongly with one phase, and Y with the other. For example, if X is an alkoxy group it can hydrolyze and react with OH groups on the surface of a filler particle.[16] Similarly, if Y is a vinyl group it can be polymerized into the organic matrix being reinforced, proving enhanced filler-matrix bonding.[16]

It is also possible to form reinforcing filler particles in situ, for example by the sol-gel hydrolysis and condensation of precursors such as organosilicates.[82] This is one of the topics covered in Chapter 8 on composite materials in general.

One reason for using extending (non-reinforcing) fillers is to reduce the cost of the compounded elastomer. They are exemplified by kaolin, diatomaceous earth, and minerals such as calcium carbonate.

Coloring agents can be either organic or inorganic, but the former can adversely affect heat stability. Examples of suitable inorganic colorants are oxides and salts of iron, chromium, cobalt, titanium, and cadmium. Some not only provide color, but can also have some beneficial heat-aging effects.

Processing aids are particularly important in the case of elastomers that contain highly reinforcing silicas, since these fillers adsorb polymer chains so strongly to their surfaces that premature gelation can occur. These additives have a softening or plasticizing effect, thus ameliorating the occurrence of this complication.[5,79]

The nature of the curing (cross-linking) agents introduced depends on the particular chemical reaction chosen for generating the cross-links.[83–86] In the case of end-linking reactions, the end groups are generally either hydroxyl or vinyl units. In the former case, the end-linking agent may be tetraethoxysilane (TEOS) [$Si(OC_2H_5)_4$], which reacts by a condensation reaction, with a stannous salt used as catalyst. In the latter case,

the end-linking agent can be an oligomeric siloxane that contains reactive Si-H groups, with the H atoms adding to the double bonds in the polymeric siloxane. Platinum salts are catalysts for this type of addition curing reaction.[83–86]

Aliphatic or aromatic peroxide curing agents can also be used, by reactions with vinyl side chains or even saturated alkyl groups. Specific peroxides are chosen on the basis of their decomposition temperatures, and the reaction products they leave behind after the curing process is complete. Some peroxides used are *bis*(2,4-dichlorobenzoyl)peroxide, benzoyl peroxide, dicumyl peroxide, and di-*t*-butyl peroxide.[83–86]

There has been some interest in cross-linking in solution, since the network chains in the subsequently dried elastomer are "super compressed." These materials can have some unusual properties, including unusually high extensibility.[87–89]

The compounding process itself can be very complicated.[5,79] The amounts of some ingredients used are fixed by the stoichiometry of the reaction in which they participate. The end-functionalized polymer and the end-linking agent are, of course, in this category. The relative amounts of other ingredients are often chosen by experience or by trial and error. After all these amounts have been selected, they are mixed ("compounded") in conventional equipment, for example a Banbury mixer. Although the resulting mixture can be fabricated immediately, it is common practice to permit the material to "recover" or "age" for a few days. If hardening occurs during this period, some remilling ("refreshening") will be required.

A variety of processing steps may then be carried out. Examples are compression molding, injection molding, transfer molding, extrusion, calendering, dispersion coating, and blowing into foams.[5,79]

Although some cures can take place at room temperature, most are carried out at elevated temperatures.[5,83–86] Conventional electric, gas or forced-air ovens are used, but presumably microwave heating could be used as well.

4.4.6 Analysis and Testing

Infrared and ultraviolet spectroscopy are often used to determine the composition of siloxane copolymers, and of mixtures of siloxanes and silicates with other species.[17,24] These types of spectroscopy can also be used to moniter (i) vinyl groups introduced to facilitate cross-linking, (ii) phenyl groups to suppress crystallization or to improve radiation resistance, or (iii) silanol end groups introduced during polymerization and used to determine number-average molecular weights, or for chemical reactions such as end linking. Some important absorbances are those for Si-O-Si groups at 1010 cm^{-1}, $Si(CH_3)_2$ groups at 800 cm^{-1}, $SiCH_3$ groups at 1260 cm^{-1}, and SiH groups at 2200 cm^{-1}. Not surprisingly, these and other methods are used for quality control in the commercial production of siloxane products.[17,24]

Nuclear magnetic resonance (NMR) is used for a variety of purposes in this area, most of which parallel those used to characterize small-molecule systems.[17,24] In addition to ^{1}H and ^{13}C NMR, ^{29}Si NMR is very frequently employed. These methods are used to characterize chemical composition, structural features, and conformational preferences. They are also used to characterize hybrid inorganic composites, and silica-type ceramics, in general.

Specific functional groups are also analyzed by chemical methods. For example, the various chlorosilanes can be hydrolyzed and the resulting chloride ions determined by

titration with silver salts. Similarly Si-H groups can be determined by measurement of the amount of hydrogen gas evolved during their hydrolyses. As a final example, silanol groups can be monitored through measurement of the amount of methane gas evolved when they are reacted with methyl Grignard reagent.[17,24]

It is, of course, possible to determine the amount of silicon present in a sample by pyrolysis to silica, followed by atomic absorption methods.

Both mass spectrometry and gas chromatography are used to identify and determine the amounts of volatile siloxane-type materials.[17,24] The more important non-volatile materials, including the polymers, can be characterized by liquid chromatography and by gel permeation chromatography (GPC), as was described in Chapter 2. When used analytically, these techniques give molecular weight distributions. Used preparatively, they yield narrow molecular weight distribution fractions that are suitable for determining reliable structure–property relationships. Average molecular weights themselves can also be determined by a variety of techniques, including dilute solution viscometry, osmometry, ultracentrifugation, and light scattering intensity measurements, as mentioned in Chapter 2. Other techniques can be used for determining molecular weight distributions, such as fractional precipitations, and gradient elutions. Extractions with super-critical fluids seem particularly promising in this regard.[90]

Thermal properties are measured and evaluated by some of the methods also mentioned in Chapter 2. For identification of transition temperatures, measurements of heats of fusion, and so on, differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are much used. Thermal stability is measured by thermogravimetric analysis (TGA), although this technique can give overly optimistic results unless used with great care.

Rheological measurements are of central importance in the processing of siloxane polymers. Typical studies would include determination of the dependence of the bulk viscosity of the material on the average molecular weight, molecular weight distribution, and rate of shear. Characterization of the effects of any branched chains or reinforcing fillers present is also of great importance.[16]

Most siloxane polymers are excellent insulators, and electrical properties relevant to this characteristic are also much studied. Examples are resistivity, dielectric constant, dielectric losses, dielectric strength (resistance to electrical breakdown), and power factors.[16]

The use of siloxane polymers in applications such as separation membranes, drug release systems, and blood oxygenators requires extensive permeability studies. This, of course, also involves measurements of diffusivity and solubility.[16]

For some specialized applications, optical properties can be of crucial importance. Two examples are contact lenses and interlayers for glass windshields. Here, transparency measurements are of primary importance, but index of refraction (n) measurements are important for matching values of n for polymers and fillers.[16,91]

Applications in the biomedical area require extensive testing of biocompatibility. These include acute, dietary, and implant testing, and monitoring toxicological effects such as carcinogenicity, mutagenicity, teratigenicity, and bacterial or fungal colonization.[16]

In the case of siloxane elastomers, the testing of mechanical properties is of particular importance. Elongation or tensile measurements are used almost to the exclusion of other types of mechanical tests, probably because of their simplicity. In this way, structural information is obtained about the networks, such as their degrees of cross-linking.[92] Measurements of the ultimate strength (modulus at rupture), and the maximum

extensibility (elongation at rupture) are also important. Relating such properties to the chemical nature of the siloxane polymer, to the curing conditions, and to the nature and amounts of any reinforcing fillers is obviously a task of paramount importance in the area of elastomeric applications.[92]

Many applications of siloxane materials involve such a complicated array of properties that the ultimate evaluation has to involve a "use" test. Many surface applications, such as release coatings, are in this category. In this approach, the prospective material is tested directly under standard conditions chosen to mimic those under which the material would actually be employed.[16,17,24] The advantage of such a test is its direct connection with the desired application. The major disadvantage results from the fact that the underlying reasons why a material fails are not uncovered in a global test of this type.

4.5 General Properties

4.5.1 Conformations and Spatial Configurations

Symmetrically Substituted Polysiloxanes

The first member of this series, poly(dimethylsiloxane) (PDMS), $[\text{-Si(CH}_3)_2\text{O-}]_x$, has been studied more extensively with regard to its configuration-dependent properties than any other chain molecule.[10,65–67,93,94] As can be seen from Figure 4.1, it is very similar in its structure to the polyphosphate chain to be discussed in Chapter 6. As was already mentioned, the Si-O bond length in polysiloxanes is 1.64 Å, and bond angles at the Si and O atoms are 110° and 143° respectively. This inequality of bond angles causes the all-*trans* form of the molecule (with rotational angles $\phi = 0°$) to form a closed structure after approximately 11 repeat units. The torsional barrier for rotations about the skeletal bonds is very low, and this is one of the reasons for the very high dynamic flexibility and very low glass-transition temperature of the PDMS chain.

Trans states are of lower energy than *gauche* states ($\phi = \pm120°$) in this chain.[10,65–67] This conformational preference may arise from favorable van der Waals interactions between pairs of CH_3 groups separated by four bonds in *trans* states. This is apparently more important than favorable coulombic interactions between oppositely charged Si and O atoms separated by three bonds, which are larger in *gauche* states because of the reduced distance. Comparisons between experimental and theoretical values of various configuration-dependent properties, however, yield a value for this energy difference that is significantly larger than that obtained from the usual semi-empirical calculations of interactions between non-bonded atoms. Conformations Involving the unlike pairs $g^{\pm}g^{\mp}$ about O-Si-O skeletal bond pairs give rise to "pentane-type interferences"[10,65–67] between the bulky $Si(CH_3)_2$ groups and are therefore completely excluded. The same conformations about Si-O-Si bond pairs cause interferences between the smaller O atoms and these can occur but to only low incidence. Such conflicting arrangements, between groups separated by four bonds, can be visualized by rotations about pairs of consecutive skeletal bonds in Figure 4.1.

There is renewed interest in relating such conformational descriptions to experimentally obtained crystal structures.[95]

The equilibrium flexibility of PDMS can be characterized by its unperturbed dimensions, in particular its value of the characteristic ratio described in Chapter 2.

Experimental values of this ratio are in the range 6.2–7.6, the precise value depending on the nature of the solvent used in the study.[10,65–67,96] The origin of this "specific solvent" effect is obscure but may involve highly specific interactions between solvent molecules and polymer segments in a way which changes the conformational preferences in the chain. The effect is significant apparently only in the case of *polar* polymers. The unperturbed dimensions appearing in the definition of the characteristic ratio also appear in the equations for the modulus of the chains when cross-linked into an elastomeric network. Not surprisingly, therefore, the specific solvent interactions can effect the modulus of swollen PDMS networks as well as the dimensions of isolated PDMS chains in solution.[92]

In any case, the characteristic ratio of PDMS is known to increase with increasing temperature. This is expected since the low energy conformation is the closed polygon mentioned above,[65–67] and increase in temperature provides thermal energy for switching from these compact, low-energy conformations to higher energy ones that are less compact. Comparisons between the experimental and theoretical values of the characteristic ratio and its temperature coefficient gave values of the chain conformational energies that were then used to predict a number of other configuration-dependent properties. Dipole moments calculated in this way were found to be in excellent agreement with experiment in the range of small chain length; the agreement at longer chain length is less satisfactory, possibly because of the large specific solvent effect[97] already mentioned. Stress-optical coefficients have also been determined for the polymer, using networks both unswollen and swollen with a variety of solvents. Only very approximate qualitative agreement was obtained, presumably because of the vanishingly small optical anisotropy of the PDMS chain.[10]

Molecular mechanics and more sophisticated computational techniques are being applied extensively to siloxane conformational problems, to study both the chain backbone and the side chains.[98]

It is interesting to note that the PDMS chain and polyphosphate chain have approximately the same characteristic ratio. Isolated *gauche* states, of relatively high spatial extension, are more prevalent in the polyphosphate chain, but *pairs* of *gauche* states ($g^{\pm}g^{\pm}$) of the same sign are less prevalent and the two effects largely offset one another.

Much experimental and theoretical work has been reported on the cyclization of dimethylsiloxane chains, and on the study of the properties of these cyclics.[68–71,99,100] The cyclization process has been investigated for a very wide range of polymer chain lengths, but only the results for the behavior of long chains will be discussed here. (The interpretation of the results for shorter chains may be complicated by failure of the Gaussian distribution function employed for the end-to-end distances, directional correlations between terminal bonds prior to cyclization, ring-strain contributions to the heat of the reaction, and the possible necessity of revising some of the statistical weight factors for the chains.) In the limit of large chain length, the agreement between theory and experiment is excellent, and thus is in strong support of the proposed model for PDMS. In addition, the cyclization studies cited have also provided useful information on excluded volume effects (their absence in the undiluted amorphous state and their magnitudes in solutions, particularly at high polymer concentrations), the critical chain length at which the Gaussian distribution becomes unacceptably inaccurate, the magnitude of specific solvent effects, and the validity of gel permeation chromatography theories pertaining to both linear and branched chain molecules.

As already mentioned, the cyclic species formed in some of these reactions are themselves of considerable interest. Their physical properties, and a comparison of them with those of the linear chains of the same degree of polymerization, have been investigated extensively.[68,69,99] Examples of such comparisons are solution viscosity–molecular weight relationships, bulk viscosities, densities, refractive indices, glass-transition temperatures, ^{29}Si NMR chemical shifts, chain dimensions from neutron scattering, diffusion coefficients and their concentration dependence, thermal stability, second virial coefficients, radii of gyration, equilibrium shapes (from Monte Carlo simulations), static dielectric permittivities, particle scattering functions, monolayer surface pressures, melting points, theta temperatures (at which the chains are unperturbed by excluded volume effects),[65] critical temperatures for phase separations, melt mobility (by excimer emission), and conformational dynamics (by ultrasonic relaxation measurements).

Other symmetrically substituted polysiloxanes have been investigated less thoroughly.[10] Poly(diethylsiloxane) $[\text{-Si}(C_2H_5)_2\text{O-}]_x$ has been reported to have a characteristic ratio of 7.7 ± 0.2, which is essentially the same value as that of PDMS. Its dipole moment is very difficult to measure because of the low polarity of the repeat unit, but it, too, is approximately the same as that of PDMS. These tentative results, if confirmed, suggest that this lengthening of the side chains must generate self-compensating effects. Furthermore, poly(di-*n*-propylsiloxane) $[\text{-Si}(C_3H_7)_2\text{O-}]_x$ has been reported to have a very large characteristic ratio, specifically, 13.0 ± 1.0. The high spatial extension in this chain could result from the fact that an articulated side chain such as $\text{-}CH_2CH_2CH_3$, could probably adopt more conformations in the form of *trans*-*gauche* states along the chain backbone than in the more restrictive *trans*-*trans* states shown in Figure 4.2. Although this "entropic destabilization" of compact *trans* states would increase the chain dimensions, so large an increase in the characteristic ratio over that for PDMS would not have been anticipated. This intuitive conclusion is supported by some rotational isomeric state calculations that do take into account the conformational variability of the siloxane side chains. It should be mentioned, however, that results of cyclization studies carried out on some stereochemically variable polysiloxanes (see below) suggest that the characteristic ratio increases with increase in length or size of the side groups.

Cyclization studies have also been carried out on the chemical copolymers poly (ethylene, dimethylsiloxane), and poly(styrene, dimethylsiloxane).[68,69,99] Numerous intramolecular interactions need to be taken into account in a chemical copolymer and,

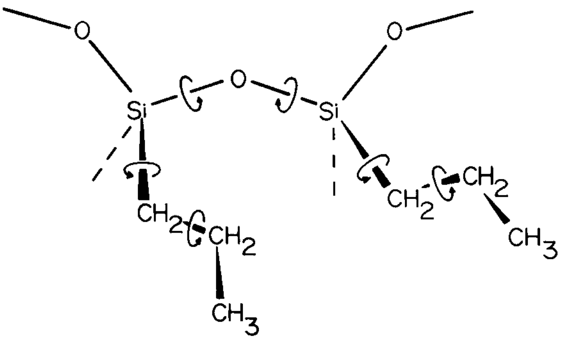


Figure 4.2 The poly(di-*n*-propylsiloxane) chain, showing the conformational variability of the propyl side chains.[10] Reproduced by permission of the American Chemical Society.

consequently, the results on the copolymers have been given only a preliminary interpretation in terms of rotational isomeric state theory. Cyclization calculations have also been carried out for poly(dihydrogensiloxane) $[\text{-SiH}_2\text{O-}]_x$, but at present there are no experimental data available for comparison with theory. Finally, melting-point depression measurements have been conducted on several symmetrically substituted polysiloxanes, specifically the dimethyl, diethyl, di-*n*-propyl, and diphenyl polymers. Interpretation of such experimental results yields entropies of fusion. Although it is very difficult to extract a reliable configurational entropy from this quantity, such results could help elucidate the configurational characteristics of the chains thus investigated.[10]

Stereochemically Variable Polysiloxanes

In these unsymmetrically disubstituted chains, the substituents of one type can be on the same side of the all-*trans* chain, on opposite sides, or on either side in a random arrangement. These are the isotactic, syndiotactic, and atactic forms first mentioned in Chapter 2. One of the chains chosen to illustrate this stereochemical variability in Figure 2.19 was, in fact, poly(methylphenylsiloxane). As already mentioned, the relatively large Si-O bond length and Si-O-Si bond angle place apposed side groups at distances of separation (ca. 3.8 Å) at which there is a favorable energy of interaction. Conformational energy calculations on this polymer indicate that the attractions should be particularly strong in the case of a pair of phenyl groups in adjacent repeat units. Therefore, the chains should have a tendency to adopt conformations in which two phenyl groups are apposed on the same side of the chain.[10] For the syndiotactic polymer this gives rise to a preference for *gauche* states, which confer relatively high spatial extension, but to a suppression of such states for the isotactic polymer. As a result, the characteristic ratio is predicted to be very small for the isotactic polymer and to increase monotonically and linearly with increases in the number of syndiotactic placements in the chain. These results are quite different from those calculated for monosubstituted $[\text{-CHRCH}_2\text{-}]_x$ vinyl or disubstituted $[\text{-CRR'CH}_2\text{-}]_x$ vinylidene chains, including the structurally analogous poly(α-methylstyrene) $[\text{-C(CH}_3\text{)(C}_6\text{H}_5\text{)CH}_2\text{-}]_x$.[10]

A characteristic ratio of 8.8 was reported for several samples of poly(methylphenylsiloxane),[10,101] at least some of which were known to be essentially atactic. This experimental result, however, can be reproduced from the model only by assuming a relatively large fraction of syndiotactic placements; the temperature coefficient predicted for this degree of syndiotacticity is then also in good agreement with experiment. The assumption of significant syndiotacticity is in disagreement with NMR results and with the results of cyclization studies, both of which suggest that poly(methylphenylsiloxane) is typically essentially atactic. The cyclization results, however, yield a prediction for the characteristic ratio that is significantly larger than the experimental value cited above. The two tentative conclusions regarding the stereochemical structure might be brought into closer agreement by improving the calculation of the interaction energy of two apposed phenyl groups to take into account the fact that they would be less exposed to favorable interactions with the solvent in such conformations. The effect is apparently quite important in polystyrene $[\text{-CH(C}_6\text{H}_5\text{)CH}_2\text{-}]_x$ but may be less so in poly(methylphenylsiloxane) because of the larger distance of separation between side groups in the siloxane polymers. Such revision could increase the number of isotactic placements that could be incorporated into the chain without

decreasing its predicted value of the characteristic ratio to below its known experimental value. In any case, resolution of this point really requires reliable experimental values of the characteristic ratio, determined on samples of known stereochemical structure.

Cyclization measurements have also been conducted on other stereochemically variable polysiloxanes $[-Si(CH_3)RO-]_x$, where R was H, CH_2CH_3, $CH_2CH_2CH_3$, and $CH_2CH_2CF_3$. The basic conclusion from these investigations was that such polymers are generally atactic in structure and that increase in the length or size of the side chains tends to increase the characteristic ratio.[68,69,99] Of course, it would be interesting to find catalysts that parallel the Zeigler–Natta catalysts used to prepare isotactic poly(α-olefin) polymers.[59] Poly(methylphenylsiloxane) samples, for example, having sufficient isotacticity (or syndiotacticity) to crystallize could be quite important. There has been very promising work based on ring-opening polymerization of cyclics of isotactic stereochemistry using catalysts that prevent scrambling of the cyclic stereochemistry during polymerization. This has yielded poly[methyl(3,3,3-trifluoropropyl)siloxane] samples ranging from the usual non-crystallizable (atactic) form, to materials that undergo strain-induced crystallization, to thermoplastics (that are crystalline at ambient temperatures).[102–104] Control of stereochemistry, in general, is an interesting and potentially important subject with regard to commercial materials.[105,106]

Some Unusual Side Groups

Including fluoro groups in the side chains of a polysiloxane can improve solvent resistance and modify surface properties,[107–109] as discussed below. Most interest has focused on replacing some hydrogens with fluorines in *n*-alkyl groups, for example the three fluorines in the trifluoropropyl group-$(CH_2)_2CF_3$. One, two, or three fluorines have also been substituted into the phenyl groups of poly(methylphenylsiloxane).[110,111]

Also of interest is the use of aromatic side groups different from the phenyl groups present in the commercially important poly(methylphenylsiloxane) or the highly intractible poly(diphenylsiloxane).[112–119] Homopolymers and copolymers having *p*-tolylsiloxane groups have been of particular interest with regard to their formation of liquid-crystalline phases.[120,121]

If the side groups are sufficiently hydrophilic, the polysiloxane can even become water soluble.[122] A final example would be the use of optically active groups as side chains, the simplest example being the *secondary* butyl group $-CH(CH_3)(C_2H_5)$. Such polymers could be studied using any of the numerous characterization techniques developed to characterize optically active polymers such as the proteins. Some of these side-group choices and their likely effects are summarized in the lower portion of Table 4.1.

Poly(dimethylsilmethylene)

This polymer, $[-Si(CH_3)_2CH_2-]_x$, can be thought of either as a hydrocarbon analogue of PDMS (in which O atoms are replaced by CH_2 groups), or as a silicon analogue to polyisobutylene $[-C(CH_3)_2CH_2-]_x$ (in which Si atoms replace one of the two skeletal C atoms in the repeat unit).[10] The polymer is shown schematically in Figure 4.3 The Si-C bonds are 1.90 Å long and, in contrast to siloxane chains, the two types of skeletal-bond angles are essentially identical and approximately tetrahedral. Most interesting is the fact that, since CH_2 and CH_3 groups have very similar interactions, this chain molecule should

Table 4.1 Some Polysiloxane Structural Changes and Expected Changes in Properties

Part of Repeat Unit	Structural Change	Expected Changes in Properties
Backbone	Replacement of O by CH_2	Decrease in polarity and tendency to cyclize
	Insertion of *p*-phenylene	Large decrease in flexibility
	Insertion of *m*-phenylene	Smaller decrease in flexibility
	Insertion of *p*-cyclohexylene	Small decrease in flexibility
	Insertion of *m*-cyclohexylene	Small decrease in flexibility
Side group	$(CH_2)_mCH_3$, $m>0$	Tendency to form liquid-crystalline phases
	Phenyl (atactic placements)	Suppression of crystallinity, and increase in radiation resistance
	Fluorinated groups	Increase in solvent resistance
	Bulky groups in general	Decrease in flexibility
	H atoms	Capacity for cross-linking by vinyl groups
	Vinyl groups	Capacity for cross-linking by H atoms
	Hydrophilic groups	Increase in water solubility
	Chiral groups, e. g., $-CH(CH_3)C_2H_5$	Generation of optical activity

have some characteristics reminiscent of the idealized "freely rotating" chain.[65–67] This conclusion is supported by experimental evidence which indicates that the characteristic ratio of the polymer is relatively small and that both its unperturbed dimensions and dipole moments are essentially independent of temperature.[10]

4.5.2 Flexibility of the Polymer Chains

Equilibrium Flexibility

The equilibrium type of flexibility mentioned above has a profound effect on the melting point T_m of a polymer, as was mentioned in Chapter 2. High flexibility in this equilibrium sense means high conformational randomness in the amorphous state, and thus high entropy of fusion and low melting point. This entropy can be reduced by a stretching process, in what is called "strain-induced crystallization," as described in Figure 2.40. The crystallites thus generated can be very important since they may provide considerable reinforcement for a network. Most polysiloxane elastomers have melting points that are unfortunately too low to benefit from this effect, however.

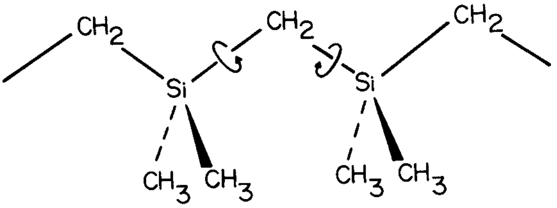


Figure 4.3 The poly(dimethylsilmethylene) chain.[10] Reproduced by permission of the American Chemical Society.

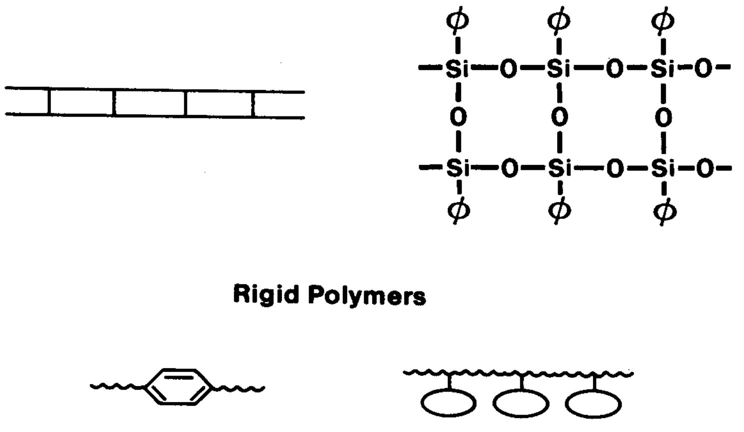


Figure 4.4 Some ways for making a polymer more rigid.[92] Reproduced by permission of John Wiley and Sons.

Examples of ways in which a polymer may be made less flexible, or more rigid, are shown in Figure 4.4.[123] They involve the combination of two chains into a ladder structure, insertion of rigid units such as *p*-phenylene groups into the chain backbone, or the addition of bulky side groups. The sesquisiloxane polymer shown in the upper portion of this figure would be in this category,[124,125] and attempts have been made to prepare it using trifunctional silanes, as shown in Figure 4.5. The basic point is to decrease the entropy of fusion and thus increase the melting point T_m (which is inversely proportional to the entropy of fusion). In this example, if the chains are combined into a ladder structure they cannot disorder themselves as much as when they are separate, as is shown in Figure 4.6. The same argument holds for the other two methods for increasing T_m. This decreased equilibrium flexibility is generally paralleled by a decreased dynamic flexibility, and thus by an increased glass-transition temperature T_g as well. Another advantage of the ladder structure is its resistance to degradative chain scission. It will not be degraded into two shorter ladder structures except in the unlikely event that two single-chain scissions occur directly across from one another.[126]

There is considerable interest in inserting a silphenylene group [-$Si(CH_3)_2C_6H_4$-] into polysiloxane backbones.[92,127–133] In the case of the PDMS repeat unit, this yields the

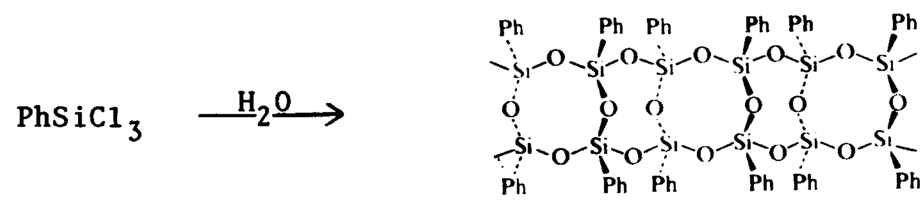


Figure 4.5 A possible reaction for preparing a sesquisiloxane ladder polymer.[52] Reproduced by permission of Prentice Hall, Inc.

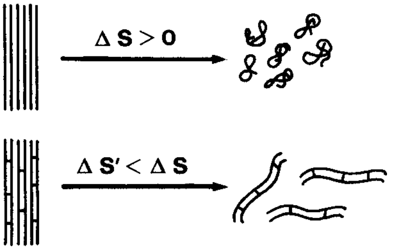


Figure 4.6 Sketch explaining the increase in melting point with increase in chain rigidity.[92] Reproduced by permission of John Wiley and Sons.

siloxane *meta* and *para* silphenylene polymers shown in Figure 4.7.[92] The T_g of the former polymer is increased to −48 °C (relative to −125 °C for PDMS) but no crystallinity has been detected to date. Since the repeat unit is symmetric, it should be possible to induce crystallinity by stretching, as described in Figure 2.40. The explanation here is the same as that given in Figure 4.6, except that the chains are prevented from completely disordering themselves by being held elongated by the stretching force, rather than by the structural features of the chains. As expected, the *p*-silphenylene group has a larger stiffening effect, increasing the T_g to −18 °C, and giving rise to crystallinity with a T_m of 148 °C. The resulting polymer is thus a *thermoplastic* siloxane. Apparently, *ortho* (*o*) silphenylene units have not been introduced in this way. They are probably much harder to incorporate because of steric problems and, even if they could be incorporated, would not be expected to have much of a stiffening effect on the chain.

Silarylene polymers that contain more than one phenylene group in the repeat unit could be of considerable interest because of the various *meta*, *para* combinations that could presumably be synthesized. Cyclohexylene (C_6H_{10}) groups can switch between

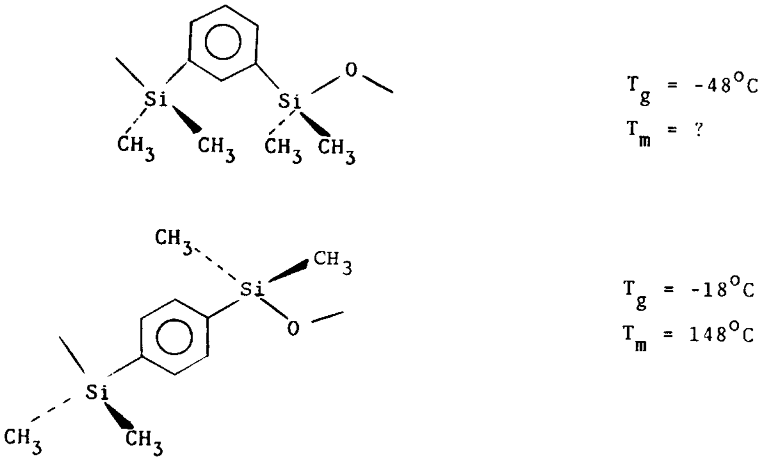


Figure 4.7 *Meta* and *para* silphenylene polymers and their transition temperatures.[92] Reproduced by permission of John Wiley and Sons.

boat and chair forms and should thus be less stiff than phenylene groups. Both *meta*- and *para* groups could be of interest in this regard. Some of these modifications and their likely effects are summarized in the upper portion of Table 4.1.

Figure 4.4 also has a sketch showing the use of bulky side groups to make a chain stiffer. This can be illustrated by replacing one of the methyl groups in the PDMS repeat unit by a phenyl group. The resulting polymer, poly(methylphenylsiloxane), has a glass-transition temperature of −28 °C, which is significantly higher than the value, −125 °C, shown by PDMS.[46]

There has been success in simulating the crystallinity of some polysiloxanes. This work was based on the model of Windle and coworkers[134] for simulating chain ordering in copolymers composed of two comonomers, at least one of which is crystallizable. Monte Carlo techniques are first used to generate chains with sequences that are representative of those occurring in the polymers of interest. In the case of chemical copolymers the generation is based on standard copolymerization equations containing the usual reactivity ratios. In the case of stereochemical copolymers, the generation is based on replication probabilities (*meso* rather than *racemic* placements). Typically, the generated chains are placed in parallel, two-dimensional arrangements. Neighboring chains are then searched for like-sequence matches that could lead to the formation of crystallites, in order to estimate extents of crystallinity.[135]

An example in the polysiloxane chemical copolymer area involved modeling random and semi-blocky poly(diphenylsiloxane-*co*-dimethylsiloxane) copolymers. In this example, the chains were placed alongside one another in a two-dimensional array, with black squares representing dimethylsiloxane (DMS) units and white squares representing diphenylsiloxane (DPS) units.[136] "Like" squares neighboring each other in the same row were then viewed as coalescing into blocks the lengths of which were compared with the known minimum length required to form a crystalline. It was thus possible to identify crystallizable DPS regions as distinct from non-crystallizable DMS component, or units of the crystallizable DPS component that were not long enough to crystallize.[136] A value of the degree of crystallinity of a simulated sample was then determined by counting the units involved in the matching sequences relative to the total number of units of all the chains. The crystallites thus identified presumably act as cross-linking sites and reinforcing domains, providing the additional toughness the semi-blocky copolymers have over their random counterparts.

An example of such modeling of a stereochemically variable polysiloxane focused on poly[methyl(3,3,3-trifluoropropyl)siloxane],[137] a polymer much studied with regard to the already-mentioned new synthetic techniques for controlling stereoregularity and thus crystallizability.[102–104,138]

It is intriguing that even some flexible siloxane polymers form mesomorphic (liquid-crystalline) phases.[34,139–166] Some illustrative data are given in Table 4.2. Both poly(diethylsiloxane) and poly(di-*n*-propylsiloxane) show two crystalline modifications as well as a mesomorphic phase. (The other major class of semi-inorganic polymers, the polyphosphazenes, are also relatively flexible, and show similarly interesting behavior.)[10,167]

Some polysiloxanes form liquid-crystalline phases because of the presence of relatively stiff side chains.[168–176] They have been much studied, particularly with regard to the effect of deformation of the elastomeric polysiloxane phase on the mesomorphic behavior exhibited by the side chains.

Table 4.2 Two Examples of Liquid-Crystalline Siloxane Polymers[a]

Polymer Repeat Unit	~T, °C	Transition
[-Si(CH_3)$_2$O-] (Reference polymer)	–40	Cryst→ Isotropic
[-Si(C_2H_5)$_2$O-]	–60	Cryst→ Cryst′
[-Si(C_2H_5)$_2$O-]	0	Cryst′→ Mesomorphic
[-Si(C_2H_5)$_2$O-]	40	Mesomorphic→ Isotropic
[-Si(*n*-C_3H_7)O-]	–55	Cryst→ Cryst′
[-Si(*n*-C_3H_7)O-]	60	Cryst′→ Mesomorphic
[-Si(*n*-C_3H_7)O-]	205	Mesomorphic → Isotropic

[a] Reproduced by permission of the American Chemical Society.

Although the polysiloxanes are much more flexible than their organic counterparts, the polysilanes seem to fall between these two extremes. In this sense, it is instructive to compare a polysilane with its hydrocarbon analogue in terms of chain flexibility. For example, relevant conformational energy calculations have been carried out on polysilane itself [-SiH_2-]$_x$.[177,178] Some conformational energies, shown as a function of two consecutive skeletal rotation angles ϕ, were in fact presented in Figure 2.23.[147] The results suggest that the lowest energy conformation should be a sequence of *gauche* states (ϕ = ±120°) of the same sign.[177,178] This is in contrast to polyethylene [-CH_2-]$_x$, which has a preference for *trans* states. Such preferences generally dictate the regular conformation chosen by a polymer chain when it crystallizes. Polyethylene crystallizes in the all-*trans* planar zig-zag conformation,[65–67] and it would be interesting to determine whether polysilane crystallizes in the predicted helical form generated by placing all of its skeletal bonds in *gauche* states of the same sign.

The calculations also predict that polysilane should have a higher equilibrium flexibility than polyethylene,[178] and solution characterization techniques could be used to test this expectation. Dynamic flexibility can also be estimated from such energy maps, by determining the barriers between energy minima. Relevant experimental results could be obtained by a variety of dynamic techniques.[179]

Dynamic Flexibility

Dynamic flexibility refers to a molecule's ability to *change* spatial arrangements by rotations around its skeletal bonds. The more flexible a chain is in this sense, the more it can be cooled before the chains lose their flexibility and mobility and the bulk material becomes glassy. Chains with high dynamic flexibility thus generally have very low glass-transition temperatures T_g.[180] Since exposing a polymer to a temperature below its T_g generally causes it to become brittle, low values of T_g can be advantageous, particularly in the case of fluids and elastomers.Structural changes that increase a chain's equilibrium stiffness generally also increase its dynamic stiffness and thus increase T_g. Conversely, the very high flexibility of PDMS is the origin of its low T_m (–40 °C)[46,181,182] as well as its very low T_g, –125 °C. [46,181,182] The general effect of increased rigidity is thus to increase a polymer's "softening temperature," which is approximately T_m if the polymer is crystalline and approximately T_g (typically ~2/3 T_m in °K) if it is not.[126]

4.5.3 Permeability

Siloxane polymers have much higher permeability to gases than most other elastomeric materials. For this reason, they have long been of interest for gas separation membranes, the goal being to vary the basic siloxane structure to improve selectivity without decreasing permeability. The repeat units of some of the polymers which have been investigated[183–188] include [-Si(CH_3)RO-], [-Si(CH_3)XO-], [-Si(C_6H_5)RO-], [-Si$(CH_3)_2(CH_2)_m$-], [-Si$(CH_3)_2(CH_2)_m$Si$(CH_3)_2$O-], and [-Si$(CH_3)_2(C_6H_4)_m$Si$(CH_3)_2$O-], where R is typically an *n*-alkyl group and X is an *n*-propyl group made polar by substitution of atoms such as Cl or N. Unfortunately, structural changes that increase the gas-diffusion selectivity are generally found to decrease the permeability, and vice versa. In addition to numerous experiments, there have been several simulations dealing with the permeability of polysiloxane membranes.[189–191] Simulations indicate that at least the asymmetrically substituted polysilanes [-SiRR′-] have gas permeabilities comparable to that of PDMS.[192] The permeability *P* is the product of the solubility *S* of the gas in the polymer and its diffusivity *D*.[193] Values of *P* for the polysilane studied seemed to be high due at least in part to very high gas solubilities in the polysilanes. It is interesting to note that these simulations indicate a much lower permeability for poly(dimethylsilmethylene) [-Si$(CH_3)_2CH_2$-].

Also of interest is the recent observation that the presence of a trimethylsilyl group [–Si$(CH_3)_3$] as a side chain in an acetylene repeat unit increases the permeability of the polymer to a value above that of PDMS! The specific polymer is poly[1-(trimethylsilyl)-1-propyne],[194–202] and some comparisons between it and PDMS are given in Table 4.3.[34] Remarkably, its permeability coefficient *P* is about an order of magnitude higher than that of PDMS without much decrease in selectivity (as measured by the ratio of the *P* values for oxygen and nitrogen). The greatly increased values of *P* are apparently due to the unusually high solubility of gases in this polymer.[195] Studies of the effects of substituting the trimethylsilyl group onto other polymer backbones are in progress.

Another type of membrane designed as an artificial skin coating for burns also exploits the high permeability of siloxane polymers.[18,203] The inner layer of the membrane consists primarily of protein and serves as a template for the regenerative growth of new tissue. The outer layer is a sheet of silicone polymer, which not only provides mechanical support, but also permits outward escape of excess moisture while preventing ingress of harmful bacteria.

Soft contact lenses prepared from PDMS provide a final example, as is shown in Figure 4.8.[34] The oxygen required by the eye for its metabolic processes must be obtained

Table 4.3 Some Gas Permeability Information[a]

Polymer Repeat Unit	Gas	10^8P^b	(P_{O_2}/P_{N_2})
[-Si$(CH_3)_2$O-]	O_2	6.0	1.9
[-Si$(CH_3)_2$O-]	N_2	3.1	—
[-C(Si$(CH_3)_3$)=C(CH_3)-]	O_2	72	1.7
[-C(Si$(CH_3)_3$)=C(CH_3)-]	N_2	42	—

[a] Reproduced by permission of the American Chemical Society.
[b] Units of cm^3(STP)cm/(cm^2 s cm Hg).

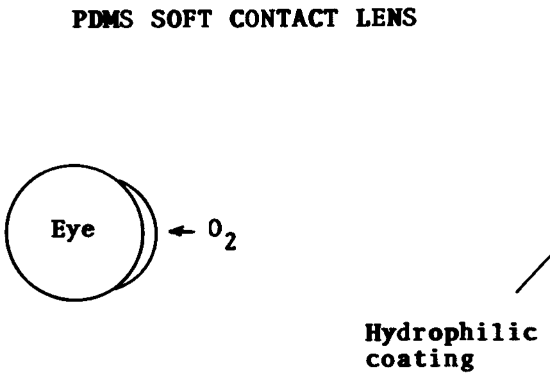


Figure 4.8 An example of the use of grafting to change only the surface properties of a polymeric material.[31] Reproduced by permission of the American Chemical Society.

by inward diffusion from the air rather than through blood vessels. PDMS is ideal for such lenses[18] because of its high oxygen permeability, but it is too hydrophobic to be adequately wetted by the fluids covering the eye. This prevents the lens from "feeling right," and can also cause very serious adhesion of the lens to the eye itself. One way to remedy this is to graft a thin layer of a hydrophilic polymer to the inner surface of the lens. Because of the thinness of the coating, the high permeability of the PDMS is essentially unaffected.

The contact lens application just cited illustrates the use of one of the most striking properties of PDMS, its superb transparency. In fact, it can retain this transparency even when filled (reinforced) with rather large amounts of silica!

4.5.4 Stability, Safety Aspects, and Environmental Impact

Siloxane polymers possess a number of properties that seem almost contradictory. One example is the tremendous stability and durability shown by polysiloxanes in a wide variety of applications.[24,204] One reason for this stability is the fact that the chain is already in a high oxidation state, and reduction takes place only at very high temperatures. Most scientists are familiar with the now-commonplace constant-temperature bath containing "silicone oil" which operates at high temperatures for years without any evidence for thermal degradation. Body implants made of polysiloxanes show little evidence of degradation, hydrolytic or otherwise, after decades of useful service, due to their resistance to hydrolysis and oxidation. (The inertness of the siloxanes should not be much of a surprise, if one thinks of them as simple hydrocarbon modifications of the silicates we commonly refer to as "glass.") In spite of this, polysiloxanes do *not* present severe environmental problems for reasons discussed below. For example, in the case of a spill, or rupture of an electrical device such as a transformer, the polymers released degrade completely and relatively rapidly under normal environmental conditions.[24,204]

Such degradation can occur in water, in air, and particularly in the soil. This occurs because the polymers come into contact with one or more reactive species that can cause their degradation. One of these is the nitrate ion present in natural waterways. It is a source of atomic oxygen, and, from it, hydroxyl radicals that initiate the degradation process. Another reagent is ozone, split by UV light into oxygen atoms, followed again by the production of hydroxyl radicals. It is interesting to note that UV light itself, has very little effect on the siloxane structure. Only the very shortest wavelengths present in sunlight have any influence and, in this case, cause generation of methyl radicals from the side groups. Polysiloxanes are resistant to all types of radiation, particularly if they contain aromatic groups, for example the phenyl groups in poly(methylphenylsiloxane).

Even when methyl radicals are replaced by silanol units, the surface of the material does not remain hydrophilic (water-wettable) very long. Either the silanol groups condense with other silanol units to restore the siloxane structure, or unmodified chain segments migrate to the surface. In any case, a “self-repair” mechanisms underlies the “recoverability” of siloxane surfaces, and this is an important part of their durability.

Clay minerals present in many soils have high surface areas with strongly acidic groups on their surfaces. These materials can react with siloxane chains and reorganize them into much smaller molecules. In fact, water readily reacts with the Si-O bond in the presence of catalytic amounts of either acids or bases. Some of these small molecules are volatile enough to evaporate into the atmosphere. Others become capped with silanol (-SiOH) groups, and this is frequently sufficient to make them water-soluble, and thus environmentally degradable. At later stages in the process, even the hydrocarbon groups are affected. Although the organosiloxane structure is completely unknown in nature, the introduction of these small molecules into the biosphere is thought to be entirely harmless. Furthermore, some of the degradation processes lead ultimately to silica, water, and carbon dioxide or inorganic carbonates.[24,204]

It will be clear that the degradative reactions experienced by siloxane chains generally generate silanol groups on the molecules, usually at their ends, and can produce various cyclics.[205] Pairs of such silanol groups can condense with one another, forming new siloxane linkages. As was mentioned above, this condensation reaction provides an interesting “healing” mechanism for the siloxane backbone.

Resistance to degradation or cross-linking by radiation is also important.[2,206] This is one advantage that poly(methylphenylsiloxane) has over poly(dimethylsiloxane); the phenyl groups are efficient energy sinks that tend to suppress the usual effects of radiation on a polymer.

There is also interest in synthesizing polysiloxanes in environmentally friendly compressed carbon dioxide.[207]

Recycling of polymers has become an important environmental issue. Not surprisingly, given its relatively high cost, such studies are underway on silicone elastomers as part of a general effort addressed to various types of elastomeric materials, including ones that are heavily filled with silica.[208–211]

4.5.5 Thermodynamics

Typical thermodynamic properties of the polysloxanes, such as heat capacities, solubility parameters, thermodynamic interaction parameters, and so on, have been extensively tabulated.[46,182,212] Of particular interest in this area are the thermodynamics of mixing,

and phase diagrams showing miscibility and phase separation among various polysiloxanes, including cyclics.[213–215] Related to phase separation is the segregation of siloxanes to surfaces in multi-phase systems because of the low surface energies of these polymers.[109,216–218] As a result, a blend or block copolymer having only a small overall percent of siloxane, can have surfaces consisting almost entirely of this minor constituent.

There is also much interest in applying various types of liquid-state theory, to PDMS in particular.[219,220]

4.5.6 Some Additional Unusual Properties of Poly(dimethylsiloxane)

Some of the unusual physical properties exhibited by PDMS are summarized in Table 4.4.[24,34,221–223] Atypically low values are exhibited for the characteristic pressure[195,196] (a corrected internal pressure, which is much used in the study of liquids), the bulk viscosity η, and the temperature coefficient of η.[2] Also, entropies of dilution and excess volumes on mixing PDMS with solvents are much lower than can be accounted for by theory.[221,222] Finally, as has already been mentioned, PDMS has a surprisingly high permeability. Another striking feature of siloxane polymers is their unusual surface properties.[14,108,224–229] Fluorosiloxane polymers[230] have been studied most recently in this regard,[107,231–233] but the properties to be described are characteristic of a number of different members of the polysiloxane family. Specifically, their surface properties permit them to serve in a variety of seemingly contradictory roles. For example, siloxanes can be both anti-foaming agents and foam stabilizers, both paper-release coatings and pressure-sensitive adhesives, both water-repellents and de-watering agents, and both emulsifiers and de-emulsifiers.[14,224] This paradox is explained by the differing ways in which the siloxane chains interact with the other species present. For example, in foam technology it is critically important whether the siloxane dissolves in the liquid phase or stays at the liquid–gas interface. Similar questions arise in other applications, and specific properties are generated by an appropriate choice of side group, addition of special polar groups, ionic groups, or reactive functional groups, or by copolymerization with completely different classes of comonomer.

Also of interest is the recent demonstration that poly(methylphenylsiloxane) can undergo a reversible droplet-monolayer transition[234] that could be very relevant to the spreading of polymers on surfaces.

Table 4.4 Some Unusual Properties of PDMS[a]

Property	Experimental Result
Characteristic pressure	Unusually small
Bulk viscosity η	Unusually small
Temperature coefficient of η	Unusually small
Entropies of dilution	Significantly lower than theory
Excess volumes on mixing	Significantly lower than theory
Permeability	Unusually large

[a] Reproduced by permission of the American Chemical Society.

In the most general terms, the unusual surface properties of polysiloxanes are due to their low surface energies and surface tensions.[14,224,235] These characteristics are then understandable in terms of two important features of the chains themselves. The first is the very low intermolecular forces between the side chains, which are the methyl groups in PDMS, the commonest of the polymers having these unusual surface properties. The second is the remarkable flexibility of the siloxane backbone, which permits the chains to easily arrange and rearrange themselves so as to place the methyl groups at their surfaces and interfaces. A particularly interesting example of this is the ease with which a damaged polysiloxane surface quickly regenerates the surface characteristics of the original material.

Although the molecular origin of the unusual properties of siloxane polymers in general is still not known definitively, a number of suggestions have been put forward. One involves low intermolecular interactions, as mentioned in the preceding paragraph. Others focus on differences between the non-polar alkyl groups and the polar Si–O backbone,[224] or the very high rotational and oscillatory freedom of the methyl side groups in PDMS, the most important of the polysiloxanes.[22] Still another focuses on the chain's irregular cross section (very large at the substituted Si atom and very small at the unsubstituted O atoms.)[222] Another possible explanation is the fact that chains with unequal skeletal bond angles would not pack as easily as those that do,[236] since they would not be able to form the planar zig-zag conformations of polymers such as polyethylene.

4.6 Reactive Homopolymers

4.6.1 Types of Reactions

In the typical ring-opening polymerization mentioned above, reactive hydroxyl groups are automatically formed at the ends of the chains.[11,61] Substitution reactions carried out on these chain ends can then be used to convert them into other reactive functional groups. These functionalized polymers can undergo a variety of subsequent reactions, some of which are listed in Table 4.5.[34] For example, hydroxyl-terminated chains, can undergo condensation reactions with alkoxysilanes (orthosilicates).[11,237] A difunctional alkoxysilane leads to chain extension, and a tri- or tetrafunctional one to network formation. Corresponding addition reactions with di- or triisocyanates provide other possibilities. Similarly, hydrogen-terminated chains can interact with molecules having active hydrogen atoms.[11,237]

Table 4.5 Reactive Siloxane Polymers[a]

$XSi(CH_3)_2O[-Si(CH_3)_2O-]_xSi(CH_3)_2X$

X	Reactant
OH	Alkoxysilanes
OH	$[Si(OC_2H_5)_4]$
H	Unsaturated groups
$CH{=}CH_2$	Active H atoms
$CH{=}CH_2$	Free radicals

[a] Reproduced by permission of the American Chemical Society

A pair of vinyl or other unsaturated groups can also be linked by their direct reactions with free radicals. Similar end groups can be placed on siloxane chains by the use of an end blocker during polymerization,[73,74] as mentioned earlier. Reactive groups such as vinyl units can, of course, be introduced as side chains by random copolymerizations involving, for example, methylvinylsiloxane trimers or tetramers.[11]

Polysiloxanes have also been pyrolyzed to give ceramics, or organic-inorganic hybrid materials.[238,239] This general topic is covered in Chapter 9.

4.6.2 Block Copolymers

One of the most important uses of end-functionalized polymers is the preparation of block copolymers.[73,74] The reactions are identical to the chain extensions already mentioned, except that the sequences being joined are chemically different. In the case of the -$OSiR_2R'Y$ chain ends mentioned above, R′ is typically $(CH_2)_{3-5}$ and Y can be NH_2, OH, COOH, CH=CH_2, and so on The siloxane sequences containing these ends have been joined to other polymeric sequences such as carbonates, ureas, urethanes, amides, and imides.

4.6.3 Hyperbranched Polymers and Dendrimers

There has long been interest in these peculiarly branched polymeric materials, and some of the most interesting species involve polysiloxane chains.[240–244]

4.7 Elastomeric Networks

4.7.1 Gelation

The gelation process that leads to the network structures required for rubber-like elasticity have been extensively studied, by experiments, theory, and simulations.[245–249] In some case, the gelation can be made to be reversible.[250]

4.7.2 Model Elastomers

The networks formed by reacting functionally terminated siloxane chains with an end linker of functionality three or greater have been used extensively to study molecular aspects of rubber-like elasticity.[53,82,92,237,251–260] They are preferred for this purpose since there are relatively few complications from side reactions during their preparation. They are "model" networks in that a great deal is known about their structure by virtue of the very specific chemical reactions used for their synthesis. For example, if a stoichiometric balance exists between chain ends and functional groups on the end-linker, the critically important molecular weight M_c between cross-links is equal to the molecular weight of the chains prior to their end-linking. Also, the functionality of the cross-links (number of chains emanating from one of them) is simply the functionality of the end-linking agent. Finally, the molecular weight distribution of the network chains is the same as that of the starting polymer, and there should be few if any dangling-chain irregularities. Since these networks have a known degree of cross-linking (as measured inversely by M_c), they can be used to test the molecular theories of rubber-like elasticity, particularly with regard to the possible

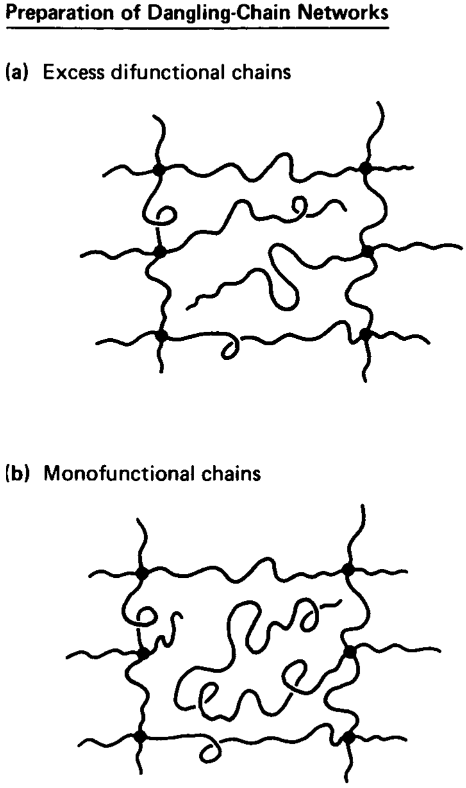


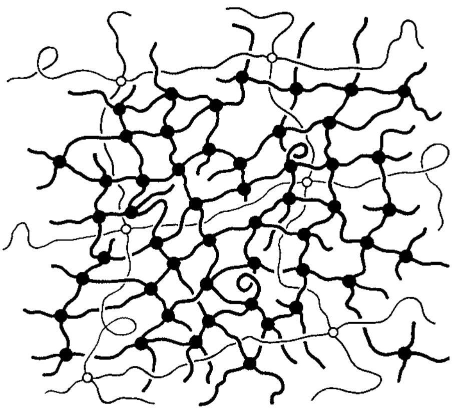
Figure 4.9 Two end-linking techniques for preparing networks having known numbers and lengths of dangling chains.[237] Reproduced by permission of the American Chemical Society.

effects of interchain entanglements.[92,237,251–258] Intentionally imperfect networks can also be prepared, as is described in Figure 4.9.[237] Such networks have known numbers and lengths of dangling chains (those attached to the network at only one end), and thus the effects of these irregularities on elastomeric properties can be determined. In the first method, the stoichiometry is unbalanced so that there is an excess of chain ends over functional groups on the end-linking molecules. The limitation in this method is the fact that the dangling chains have to have the same average length as the elastically effective chains (those attached to the network at both ends). The second method avoids this limitation by the use of monofunctionally terminated chains of whatever length is desired.

These reactions can also be used to form networks that interpenetrate,[18,237,261–267] as illustrated in Figure 4.10.[237] For example, one network could be formed by a condensation end-linking of hydroxyl-terminated short chains and the other by a simultaneous but independent addition end-linking of vinyl-terminated long chains. Interpenetrating networks are of interest because they can be unusually tough, and could have unusual dynamic mechanical properties.

One of the most interesting types of model networks is the bimodal. These networks consist of very short chains intimately end-linked with the much longer chains that are representative of elastomeric materials.[237,251,253,268–278] Such a network is shown in Figure 4.11,[269] where the short chains are arbitrarily drawn thicker than the long ones.

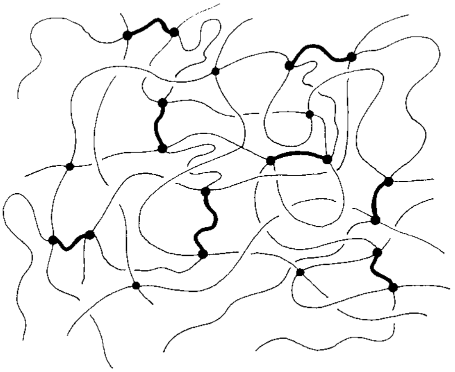
Figure 4.10 Sketch of two interpenetrating networks.[237] Reproduced by permission of the American Chemical Society.



These materials have unusually good elastomeric properties, specifically, large values of both the ultimate strength and maximum extensibility. Possibly, the short chains contribute primarily to the former, in that their very limited extensibilities should give very high values for the modulus. The long chains might then contribute primarily by increasing the maximum extensibility, by somehow delaying the spread of the rupture nuclei necessary for catastrophic failure of the material. Monte Carlo simulations based on a rotational isomeric state model,[279,280] as well as analytical calculations,[281] have helped elucidate the molecular origins of this interesting type of reinforcement.

An additional bonus exists if the chains in the bimodal network readily undergo strain-induced crystallization.[92,274,278,282] It has been observed that the extent to which the bimodal networks are superior to their unimodal counterparts is larger at lower temperatures. This indicates that the bimodal character of the chain length distribution facilitates strain-induced crystallization. Apparently the short chains increase the orientation of the long chains, and this facilitates the crystallization process.

Figure 4.11 Sketch of a bimodal network.[269] Reproduced by permission of Huthig and Wepf Verlag.



Because of the improvements in properties exhibited by elastomers having bimodal distributions,[82] there have been attempts to prepare and characterize "trimodal" networks.[283] Although experiments have been carried out to evaluate the mechanical properties of trimodal elastomers, this has not been done in any organized manner. The basic problem is the large number of variables involved, specifically, three molecular weights and two independent composition variables (mol fractions); this makes it practically impossible to do an exhaustive series of relevant experiments. For this reason, the only mechanical property experiments that have been carried out have involved arbitrarily chosen molecular weights and compositions.[284–286] Perhaps not surprisingly, only modest improvements have been obtained over the bimodal materials.

Some recent computational studies,[287] however, indicate that it is possible to do simulations to identify those molecular weights and compositions that should maximize further improvements in mechanical properties. Results to date[283] suggest that a trimodal network prepared by incorporating small numbers of very long chains into a bimodal network of long and short chains could have significantly improved ultimate properties.

There is increasing interest in simulations to better understand the structures[288] and deformations of polysiloxane networks in general.[289,290]

Also, not only do short chains improve the ultimate properties of elastomers, but long chains improve the impact resistance of the much more heavily cross-linked thermosets.[271]

4.7.3 Trapping of Cyclic Oligomers

If relatively large PDMS cyclic oligomers are present in reaction systems where linear PDMS chains are being end-linked, then some of the cyclic species will be permanently trapped by one or more network chains threading through them.[291] This is illustrated by cyclics B, C, and D in Figure 4.12.[292] One interesting result is the observation that the percent cyclic trapped does not depend on the amount of time elapsed between mixing

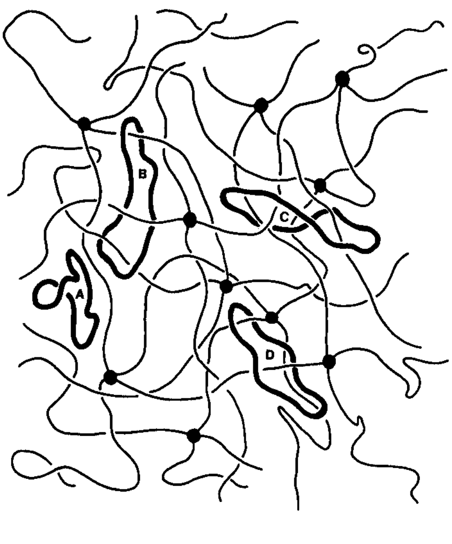


Figure 4.12 Sketch of the trapping of cyclics during the end-linking preparation of a network.[292] Reproduced by permission of the American Chemical Society.

the two components and the end-linking of the linear chains. This is certainly consistent with the very high mobility of siloxane chains, as already described. In any case, interpretation of the fraction trapped as a function of ring size, using rotational isomeric theory and Monte Carlo simulations, has provided useful information about the spatial configurations of cyclic molecules, including the effective hole size they present in the undiluted, amorphous state.[292]

This technique can also be used to form a network that has no cross-links whatsoever. Mixing linear chains with large amounts of cyclics and then *d*iunctionally end-linking them can give sufficient cyclic interlinking to yield a "chain mail" or "Olympic" network,[293–295] as is illustrated in Figure 4.13.[294] Such materials could have very unusual equilibrium mechanical properties. For example, they might deform, at least in part, by a mechanism very different from that for more conventional elastomers (the entropy-decreasing stretching out of the network chains). Their dynamic mechanical properties could well be intriguingly different also.

4.8 Some New Characterization Techniques Useful for Polysiloxanes

4.8.1 Optical and Spectroscopic Techniques

An example of a relevant optical property is the birefringence of a deformed polymer network.[256] This strain-induced birefringence can be used to characterize segmental orientation, and both Gaussian and non-Gaussian elasticity.[92,296–302] Infrared dichroism has also been particularly helpful in this regard.[82,303] In the case of the crystallizable polysiloxane elastomers, this orientation is of critical importance with regard to strain-induced crystallization, and the tremendous reinforcement it provides.[82]

Other optical and spectroscopic techniques are also important, particularly with regard to this segmental orientation. Some examples are fluorescence polarization, deuterium nuclear magnetic resonance (NMR), and polarized infrared spectroscopy.[92,256,304]

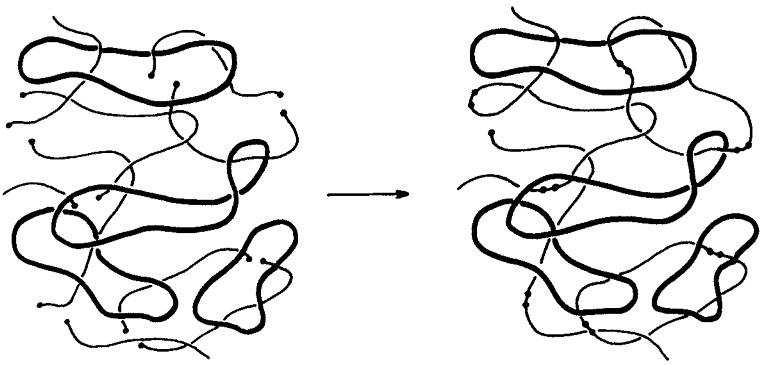


Figure 4.13 Preparation of a "chain mail" or "Olympic" network consisting entirely of inter-looped cyclics.[294] Reproduced by permission of Butterworth.

4.8.2 Microscopies

A great deal of information is now being obtained on filler dispersion and other aspects of elastomer structure and morphology through the use of scanning probe microscopy, which consists of several approaches.[52,305–309] One approach is that of scanning tunneling microscopy (STM), in which an extremely sharp metal tip on a cantilever is passed along the surface being characterized while measuring the electric current flowing through quantum mechanical tunneling. Monitoring the current then permits maintaining the probe at a fixed height above the surface, and display of probe height as a function of surface coordinates then gives the desired topographic map. One limitation of this approach is the obvious requirement that the sample be electrically conductive.

Atomic force microscopy (AFM), on the other hand, does not require a conducting surface. The probe simply responds to attractions and repulsions from the surface, and its corresponding downward and upward motions are directly recorded to give the relief map of the surface structure. The probe can be either in contact with the surface, or adjacent to it and sensing only coulombic or van der Waals forces.

An example of an application to polysiloxane elastomers is the characterization of binodal and spinodal phase-separated structures occurring in model PDMS networks.[310–312]

4.8.3 Nuclear Magnetic Resonance

Although nuclear magnetic resonance (NMR) has been used to characterize some aspects of polymerizations (for example, copolymerization kinetics),[313] the applications most relevant here have to do with characterizing structure. In this regard, NMR has been much used to study the characteristics of cross-linked polymers, including the polysiloxanes, particularly with regard to orientations,[314] molecular motions,[315–320] and their effects on the diffusion of small molecules.[321–323] Aspects related to the structures of the networks include the degree of cross-linking,[324–326] the distributions of cross-links,[327,328] and stresses,[329] and topologies.[330–332] Another example is the use of NMR to clarify some issues in the areas of aging and phase separation.[333]

Most elastomers require reinforcing fillers to function effectively, and NMR has been used to characterize the structures of such composites as well. One examples is the adsorption of chains onto filler surfaces,[334,335] and the strong absorption of these chains into "bound rubber," for example PDMS immobilized onto high surface area silica.[316,320] Another example is the use of NMR to image the filler or polymer itself.[336–342]

4.8.4 Small-Angle Scattering

Some small-angle X-ray scattering techniques have also been applied to polysiloxane elastomers. One examples is the characterization of the structures of gels.[343] The most important example, however, has been the characterization of fillers precipitated into polysiloxane elastomers, and the corresponding incorporation of such elastomers into ceramic matrices (in both cases to improve mechanical properties).[92,344,345] Some of this work is described in Chapter 8.

The chain dynamics of PDMS have also been studied by quasielastic neutron scattering.[346]

4.8.5 Brillouin Scattering

The application of Brillouin scattering to the characterization of PDMS networks was found to be useful for looking at glassy-state properties of such elastomers at very high frequencies.[347,348]

4.8.6 Pulse Propagation

Another example of a relatively new technique for the non-invasive, non-destructive characterization of network structures involves pulse-propagation measurements.[349,350] The goal here is the rapid determination of the spacings between junctions and between entanglements in a network structure. In this technique, the delay in a pulse passing through the network is used to obtain such information on the network structure.[347]

Ultrasonic methods have also been used to study interdiffusion between two samples of PDMS differing only in molecular weight.[351]

This list is essentially an extension of parts of Chapter 2, and many of the techniques described here are also useful for characterizing the composites described in Chapter 8.

4.9 Copolymers and Interpenetrating Networks

4.9.1 Random Copolymers

These materials may be prepared by the copolymerization of a mixture of cyclic oligomers rather than by the homopolymerization of a single type of cyclic.[11,61,113,352,353] Although the resulting polymer can be quite blocky, taking the reaction to equilibrium can give a polymer that is essentially random in its chemical sequencing.[74,352] One reason for preparing copolymers is to introduce functional species, such as hydrogen or vinyl side groups, along the chain backbone to facilitate cross-linking. Another reason is the introduction of sufficient chain irregularity to make the polymer inherently non-crystallizable.

4.9.2 Block Copolymers

As already mentioned, the sequential coupling of functionally terminated chains of different chemical structure can be used to make block copolymers,[59,354,355] including those in which one or more of the blocks is a polysiloxane.[74,115,356] If the blocks are relatively long, separation into a two-phase system almost invariably occurs. Frequently, one type of block will be in a continuous phase and the other will be dispersed in it in domains having an average size the order of a few hundred angstroms. Such materials can have unique mechanical properties not available from either species when present simply in homopolymeric form. Sometimes similar properties can be obtained by the simple blending of two or more polymers.[357]

4.9.3 Interpenetrating Networks

In this type of material, two networks are formed, either simultaneously or sequentially, in such a way as to interpenetrate one another. They thus "communicate" with one another through interchain interactions, including entanglements, rather than through

covalent bonds. A particularly simple example would be the already-mentioned simultaneous formation of two PDMS networks, one by a condensation end-linking reaction and the other by an addition end-linking reaction, with the two types of chains mixed at the molecular level.[264]

A more complex example, with more novel properties, is the preparation of interpenetrating networks (IPNs) between PDMS and an organic thermoplastic polymer such as a Nylon, polyurethane, or polyester. The preparation of this material, called Rimplast® by its developers,[18] involves a chemical reaction between a vinyl-functional polysiloxane blended into the thermoplastic, and a hydride-functional PDMS blended into more of the same thermoplastic. Small amounts of platinum catalyst are also present in both types of components. The amounts of polysiloxane present are typically around 10%. Pellets of both components are placed in an extruder or other high-temperature processor, where they melt into a uniform mass, at approximately 300 °C. The reaction between the two complementary types of PDMS results in a network evenly distributed throughout the thermoplastic in a type of "semi-IPN" (containing only one type of network, from the PDMS). The advantage of the resulting composite material is the fact that it has the good properties of both the PDMS (good lubricity, abrasion resistance, and dielectric properties), and the thermoplastic (good mechanical strength and molding characteristics).

4.10 Applications

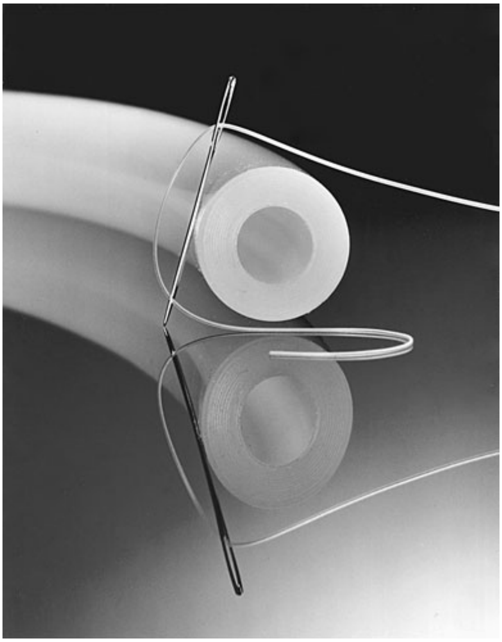
4.10.1 Medical

Numerous medical applications have been developed for siloxane polymers.[11,18,22,358] Prostheses, artificial organs, objects for facial reconstruction, vitreous substitutes in the eyes, and tubing and catheters, for example, take advantage of the inertness, stability, and pliability of the polysiloxanes. Artificial skin, contact lenses, and drug-delivery systems utilize their high permeability as well. Such biomedical applications have led to extensive biocompatability studies,[359,360] particularly on the interactions of polysiloxanes with proteins.[361] There has been considerable interest in modifying these materials to improve their suitability for biomedical applications in general.[362,363] Advances seem to be coming particularly rapidly in the area of high-tech drug-delivery systems.[364,365]

Figure 4.14 shows the range of diameters of Silastic medical-grade siloxane tubing available for medical applications. The smallest tubing has an internal diameter of only 0.012 inches (0.031 cm) and an outer diameter of only 0.025 inches (0.064 cm)! Such materials must first be extensively tested, including sensitization of skin, tissue cell culture, and implant studies. There has been considerable controversy over the safety of using polysiloxanes in breast implants.[366,367] The major concern was "bleeding" of low molecular weight polysiloxanes out of the gels in the implant into the chest cavity, followed by transport to other parts of the body. The questions of the extent to which this occurred and its possible systemic effects on the body were argued vigorously in the media and in the courts, and led to restrictions on their use.

In the case of controlled drug-delivery systems, the goal is to have the drug released at a relatively constant rate (zero-order kinetics) at a concentration within the therapeutic range. It is obviously important to minimize the amount of time the concentration is in

Figure 4.14 Siloxane polymer used in tubing and catheters for medical applications. The photograph was generously provided by the Dow Corning Corporation of Midland, MI.



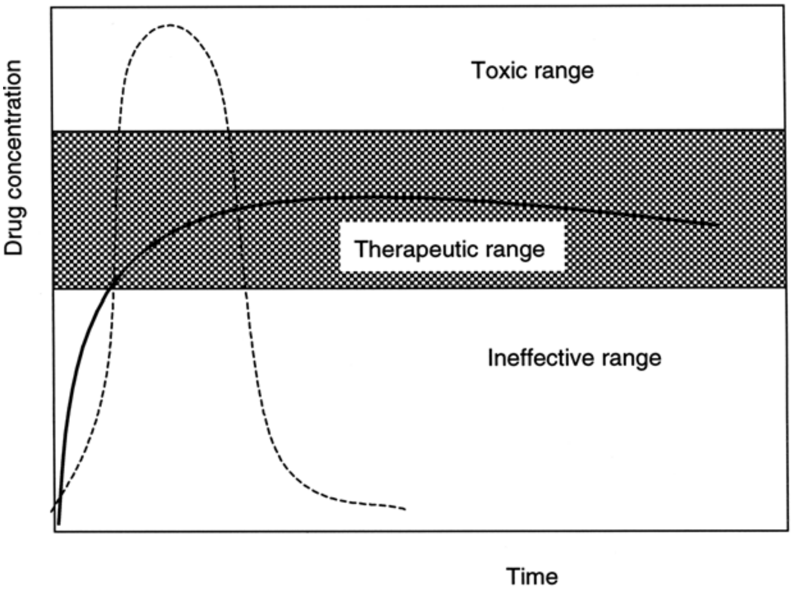


Figure 4.15 Drug concentrations in the body as a function of time. The dashed line shows the uncontrolled dissolution of a pill, with two regions so low that the concentration would be ineffective, and another region possibly high enough to be toxic. The solid line shows the goal of controlled delivery, specifically a relatively constant delivery rate in the therapeutic range for an extended period of time.

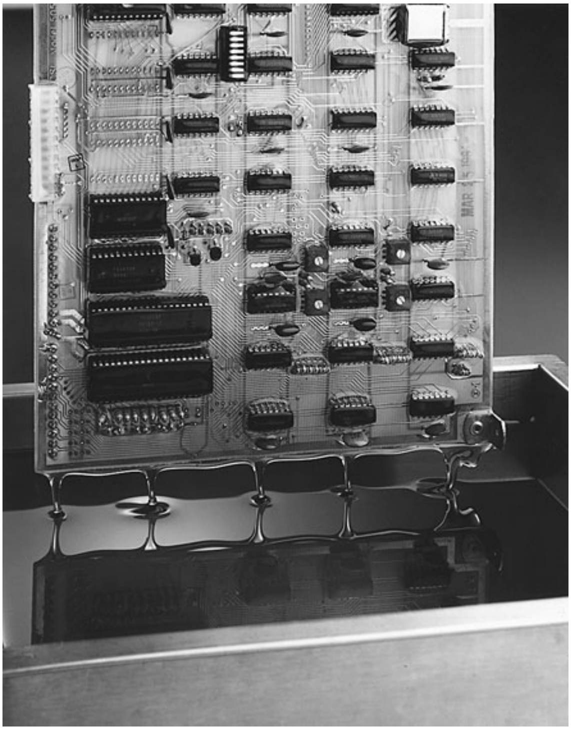
the low, ineffective range, and to eliminate completely the time it is in the high, toxic range. This is illustrated in Figure 4.15, and the use of polysiloxanes specifically in such drug-delivery systems is illustrated in Figure 4.16. The goal mentioned is approached by placing the drug inside a siloxane elastomeric capsule, which is then implanted in an appropriate location in the body. The drug within the capsule can be either in the free state, in a fluid suspension, or mixed or dissolved into an elastomeric matrix. Release rates for drugs that are much more hydrophilic than the polysiloxanes, for example melatonin and sulfanilamide, are frequently relatively slow. They can be increased, however, by incorporating solvents, channeling agents, or fillers in the capsule.

4.10.2 Non-Medical

Typical non-medical applications include high-performance elastomers, membranes, electrical insulators, water repellents, anti-foaming agents, mold-release agents, adhesives, protective coatings,[368] release control agents for agricultural chemicals, encapsulation media, mold-making materials, coatings, layers in high-tech laminates, and hydraulic, heat transfer, and dielectric fluids.[11,22,369–371] These applications are based on the same properties of polysiloxanes just mentioned and also their ability to modify surfaces and interfaces (for example as water repellents, anti-foaming agents, and mold-release agents). In some cases the polysiloxane is blended into a material to improve its mechanical properties, for example its impact strength. For such applications, finely-divided cross-linked powders are available commercially.[372,373] Two additional examples are the uses of polysiloxanes in polymer-electrolyte complexes,[374] and in microlithographic applications.[375]

Figure 4.16 A controlled release drug-delivery system that utilizes both siloxane elastomers and fluids. The photograph was generously provided by the Dow Corning Corporation of Midland, MI.

Figure 4.17 An electronic circuit board being given a protective polysiloxane coating. The photograph was generously provided by the Dow Corning Corporation of Midland, MI.



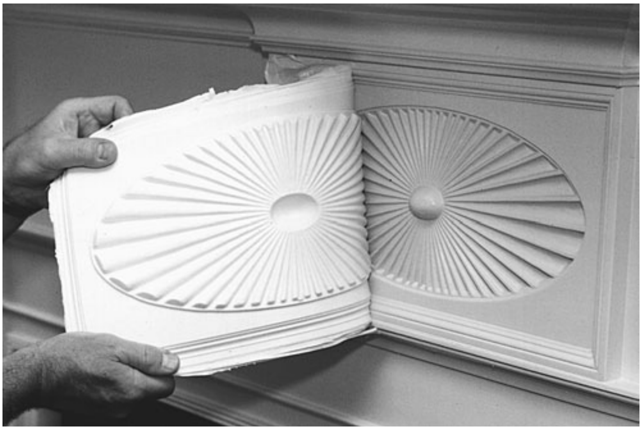


Figure 4.18 A polysiloxane Room-Temperature Vulcanizate (RTV) being used to make a mold of an intricately carved surface. The photograph was generously provided by the Dow Corning Corporation of Midland, MI.

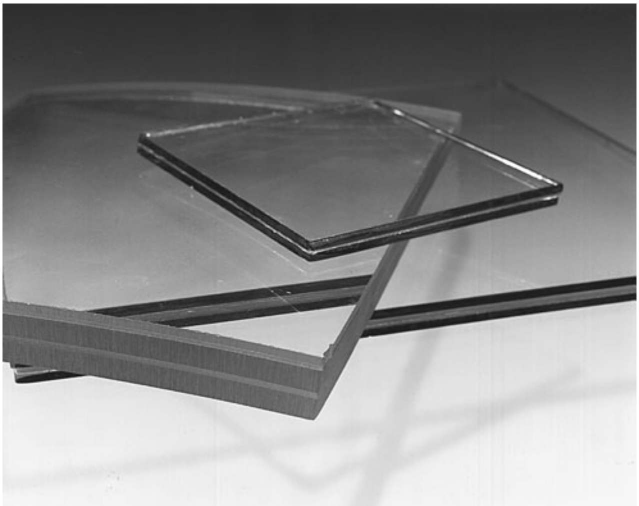


Figure 4.19 High-transparency polysiloxane elastomer used as a stress-relieving inter-layer in the type of safety glass or plastic used in windshields and canopies. The photograph was generously provided by the Dow Corning Corporation of Midland, MI.

Figure 4.17 shows a typical non-medical application of a siloxane polymer. In this case, a liquid, UV-curable polysiloxane is being used to protect a printed circuit board. The polymer being used was specifically chosen for its low viscosity, moisture resistance, and easy repairability. Also, some such materials can be treated so that thin spots in the coating are readily apparent. Although dip coating is illustrated in the figure, flow coating and spray coating can also be used.

One of the most impressive applications of polysiloxanes, particularly in the arts, is their use in making molds of intricate surfaces. This is illustrated in Figure 4.18. In this case, the surface to be copied was vertical and non-movable, so a "non-slumping" end-linkable paste had to be used rather than a liquid. After the surface was coated, it was cured to give a remarkably faithful reproduction that was easily removable from the original surface.

In another example, a polysiloxane appears as an inter-layer in the types of plastic and glass laminates used for increased safety in windshields and canopies in aircraft. The flexibility and thermal stability of these polymers are great advantages in the case of high-performance aircraft, which can experience wide variations in temperature. In this application, a polysiloxane is chosen to give the highest transparency and good adhesion to the plastic or glass outer layers. The excellent transparency of such composites is readily seen in the samples displayed in Figure 4.19.

Polysiloxanes are apparently the materials of choice in the new "soft-lithography" techniques.[376–380] The method is outlined briefly in Figure 4.20. In the first step, linear (liquid) PDMS is poured over the surface of the master to be reproduced. It is then cross linked, and peeled away from the master surface. The PDMS surface containing the pattern is then coated with a hydrophobic alkane thiol, and the pattern transferred to a

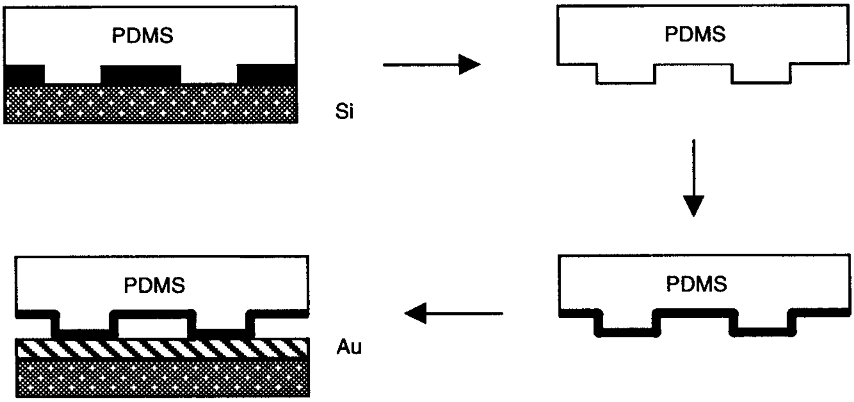


Figure 4.20 Steps in soft lithography. The PDMS in the beginning sketch is first cross-linked, then removed, and then coated with a thiol that transfers the original pattern to a gold layer.

gold surface (to which the thiol strongly binds). The pattern placed onto the gold surface can then be developed using a variety of techniques, including washing with a hydrophilic thiol to coat those parts of the surface not covered by the hydrophobic thiol. The advantages of PDMS in this area are (i) high fluidity (which is required to make good replicas of the master), (ii) ease of cross-linking at ambient temperatures (to make the features of the stamp permanent), (iii) superb elasticity and robustness (for removing the PDMS stamp and using it in microcontact printing), and (iv) excellent stability (for long-term storage of patterns).

A final mention should be made of the use of polysiloxanes in the area of microfluidics.[377,381] Devices of this type have to have channels or capillaries with dimensions 10–10,000 μm, and their preparation is relatively straightforward with PDMS, using the soft-lithography techniques just described to make the required molds.

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5

Polysilanes and Related Polymers

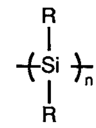
5.1 Introduction

In polysilane polymers, the polymer backbone is made up entirely of silicon atoms. Therefore these materials differ from other important inorganic polymers, the siloxanes and phosphazenes, in which the polymer chain is heteroatomic. Structurally, they are more closely related to homoatomic organic polymers such as the polyolefins. However, because the units in the main chain are all silicon atoms, the polysilanes exhibit quite unusual properties. The cumulated silicon-silicon bonds in the polymer chain allow extensive electron delocalization to take place, and this delocalization of the sigma electrons in the Si-Si bonds gives the polysilanes unique optical and electronic properties. Many of the potential technical uses, as well as the remarkable properties, of polysilanes result from this unusual mobility of the sigma electrons.

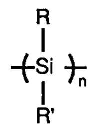
The polysilanes can be regarded as one-dimensional analogs to elemental silicon, on which, of course, nearly all of modern electronics is based. The photophysical behavior of polysilanes is not approached by any other materials, save for the less stable and more costly polygermanes and polystannanes. The remarkable properties of polysilanes have led to intense interest, and to numerous proposed high-tech applications. But the great promise of polysilanes as materials has yet to be realized. Their only commercial use at present is as precursors to silicon carbide ceramics, an application which takes no advantage of their optical or electronic properties.

Linear polysilane polymers, properly called poly(silylene)s, can be obtained as homopolymers or copolymers. Continuation of the polysilane chain consumes two of the four valences of each silicon atom; the other two are taken up by pendent groups, which may be the same (**5.1**) or different (**5.2**). Copolymers (**5.3**), which contain two or more kinds of silicon atoms, can be made up from units like those in **5.1** or **5.2**. A typical example is the copolymer of Me_2Si and PhMeSi units,

poly(dimethylsilylene-*co*-phenylmethylsilylene) (**5.4**), which bears the popular name "polysilastyrene." The pendent groups are typically organic units and can include alkyl, aryl, substituted aryl, hydrogen, Me_3Si, ferrocenyl, and so on. An unlimited number of different polymers are possible, and several hundred compositions have been described in the literature.



5.1



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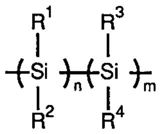

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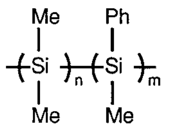


5.4

The properties of the polysilanes, like those of the polyphosphazenes, depend greatly on the nature of the substituent groups. Polysilanes cover the entire range of properties from highly crystalline and insoluble, through partially crystalline, flexible solids, to glassy amorphous materials and rubbery elastomers.

Until recently, it was thought that polysilanes would be either intractable or unstable. In his famous book, Eugene G. Rochow, the father of the silicone industry, dismissed polysilane polymers in this way:

> It follows that, even though suitable procedures were to be found for the alkylation of longer silicon chains, the products would be subject to oxidation, to thermal dissociation, and to hydrolysis in the presence of alkalies. It seems unlikely that any combination of substituents could stabilize these chains sufficiently to allow their practical application to polymeric materials.[1]

Yet we know now that polysilane polymers are stable to heat up to almost 300 °C, are inert to oxygen at ordinary temperatures, and are only mildly susceptible to hydrolysis. The principal weakness of polysilanes, as materials, is not any of these properties; it is that they become degraded when exposed to ultraviolet light.

Undoubtedly, Rochow thought of the polysilanes as structural polymers like the polysiloxanes, and never envisioned that polysilanes might have other sorts of uses. But today, polysilanes are being investigated for numerous technological applications. Polysilanes show considerable promise as ultraviolet-acting photoresists for microelectronics, and as photoconductors in electrophotography; they are active as free-radical photoinitiators for organic reactions and show marked non-linear optical properties which may make them useful in laser and other optical technology. These potential practical uses for polysilanes will be discussed later in this chapter, in Section 5.13.

5.2 History

Oligomeric phenylpolysilanes, including the perphenylated rings $(Ph_2Si)_n$, $n = 4$–6, were studied more than 80 years ago by F. S. Kipping and his students,[2] but high polymers were almost unknown until the late 1970s, and the belief that silicon had limited capability for catenation persisted until quite recently.

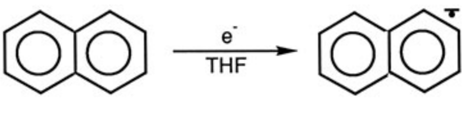
The first clear description of a polysilane polymer appears in a classic paper by C. A. Burkhard of the General Electric Co. Laboratories published in 1949.[3]

Burkhard combined one pound of sodium metal with 700 mL of dimethyldichlorosilane and heated the mixture in a steel autoclave to make poly(dimethylsilylene), $(Me_2Si)_n$ (equation (1)). This polymer is a highly crystalline material, which decomposes above 250 °C without melting and is essentially insoluble in all organic solvents. Although we know now that $(Me_2Si)_n$ is atypical among polysilanes, Burkhard's description left no doubt that $(Me_2Si)_n$ is quite intractable, and this perhaps contributed to the neglect suffered by the polysilanes over the next three decades.

$$Me_2SiCl_2 + 2Na \longrightarrow (Me_2Si)_n + 2NaCl \qquad (1)$$

Even though polysilane high polymers were largely ignored between 1949 and 1975, fundamental studies on linear and cyclic oligosilanes were being carried out in several laboratories. The linear permethylpolysilanes, $Me(SiMe_2)_nMe$ (n = 2–12), surprisingly were found to have strong ultraviolet absorption bands, which became more intense and shifted to longer wavelength as the number of Si atoms in the chain increased.[4] This behavior is reminiscent of that found for conjugated polyenes and was the first indication that electrons in the silicon-silicon bonds of polysilanes might be delocalized.

The cyclic peralkylsilane oligomers, $(R_2Si)_n$ with n = 4–6, manifested especially strong electron delocalization.[5] These rings are structurally analogous to those of the cycloalkanes, since the silicon atoms form four sigma bonds. However, the electronic properties of the cyclosilanes more nearly resemble those of aromatic hydrocarbons such as benzene. One example of such behavior is their reduction to anion radicals. Aromatic hydrocarbons such as naphthalene can be reduced, electrolytically or with alkali metals, to deeply colored anion radicals in which an unpaired electron occupies the lowest unoccupied molecular orbital (LUMO) of the hydrocarbon (equation (2)).



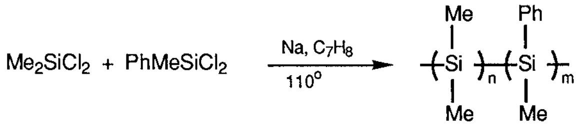
Colorless Green (2)

Since they contain an unpaired electron, anion radicals can be studied by electron spin resonance spectroscopy. The cyclosilanes $(RR'Si)_n$, where n = 4–6, similarly undergo reduction to strongly colored anion radicals whose electron spin resonance spectra indicate that the unpaired electron is completely delocalized over the ring (equation (3)). Cyclosilanes are synthesized by alkali metal reduction of diorganodichlorosilanes, usually in ethereal solvents. One outgrowth of the study of these compounds was the finding that under non-equilibrium conditions, large rings may be formed, containing up to 40 silicon atoms.[6] Although their molecular weights are not very high, these compounds may be considered as early examples of polysilane polymers.

$$\underset{\text{Colorless}}{(Me_2Si)_5} \xrightarrow[-60^\circ]{e^-,\ THF} \underset{\text{Blue}}{(Me_2Si)_5^{\bar{\cdot}}} \qquad (3)$$

Interest in polysilanes was aroused in 1975, when Yajima found that the permethyl polymer $(Me_2Si)_n$, or its cyclic oligomer $(Me_2Si)_6$, could be transformed into silicon

carbide by heating to high temperatures.[7] Shortly after this, in the course of an attempt at Wisconsin to make cyclic oligosilanes containing phenyl and methyl groups, Me_2SiCl_2 and $PhMeSiCl_2$ were cocondensed with sodium metal (equation (4)). Instead of the desired ring compounds the product was mainly a linear polymer, but unlike the permethyl polymer described earlier, this copolymer was meltable and quite soluble in organic solvents.[8,9] Evidently, the introduction of phenyl groups along the chain greatly reduces the crystallinity so that the polymer becomes thermoplastic and soluble. Soluble polysilane polymers were discovered independently at Union Carbide Corporation[10] and Sandia Laboratories[11] at almost the same time.



(4)

The growth of interest in poly(silylene)s is indicated in Figure 5.1, which shows the number of literature publications on polysilanes (and oligosilanes) plotted versus time. Note that few publications appeared before 1980, but during the past 20 years scientific activity in this field has increased dramatically. The interest in polysilanes stems partly from their novel constitution and behavior and partly from their potential utility. The possibility that soluble polysilanes might be precursors to silicon carbide was evident when they were first synthesized, but other technological uses were not so obvious and arose only in the course of research.

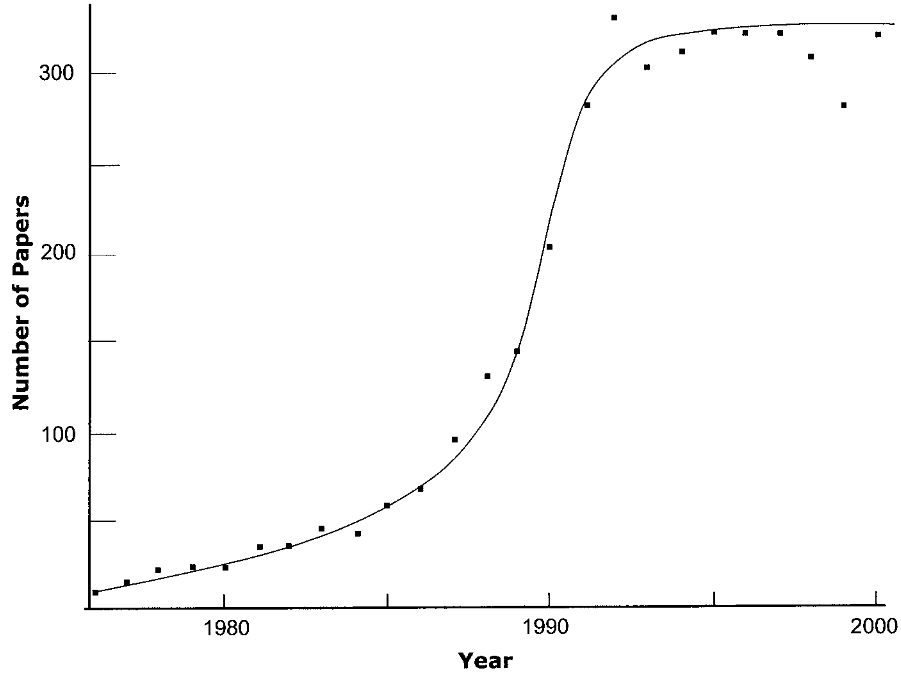


Figure 5.1 Number of papers published on polysilane polymers and oligomers per year, plotted against time, showing the dramatic growth in the literature since 1984.

5.3 Synthesis

5.3.1 Condensation of Dichlorosilanes with Alkali Metals

Polysilanes are usually made by dehalogenation of diorganodichlorosilanes with sodium metal in an inert diluent, following essentially the original method of Burkhard.[3] Single dichlorosilanes yield homopolymers, while mixtures of dichlorosilanes lead to copolymers (equations (5), (6)). For many polysilanes, good results are obtained using finely divided sodium, above its melting point, 98 °C.[12] The sodium may be added as a preformed dispersion, or dispersed by vigorous stirring in the diluent. Toluene is convenient as a diluent because its boiling point of 111 °C allows the reaction to be carried out at reflux temperature. An efficient condenser is required because the heat of reaction is substantial. Other solvents such as alkanes (decane) or ethers (diglyme) may be used, either alone or mixed with toluene or xylene. Often the chlorosilane(s) are added slowly to the stirred sodium and diluent, but the reaction can also be carried by "inverse addition" in which preformed sodium dispersion is added to a stirred solution of the chlorosilane(s). Potassium metal, or sodium-potassium alloy, or potassium-graphite may be used in place of sodium with many chlorosilanes. Electrochemical reduction of dichlorosilanes is also possible; good yields of poly(arylalkyl)silanes are reported from the electroreduction of dichlorosilanes using a magnesium cathode.[13]

$$RR'SiCl_2 \xrightarrow[> 100^{\circ}C]{Na,\ solv.} (RR'Si)_n \qquad (5)$$

$$R^1R^2SiCl_2 + R^3R^4SiCl_2 \xrightarrow[> 100^{\circ}C]{Na,\ solv.} (R^1R^2Si)_n(R^3R^4Si)_n \qquad (6)$$

Ultrasound activation accelerates the synthesis, probably by maintaining a clean surface on the sodium particles. This allows the Wurtz synthesis to be carried out at much lower temperature, in benzene, tetrahydrofuran (THF) or diethyl ether.[14] The synthesis is also speeded by the addition of additives which complex alkali metal cations, that is 15-crown-5 ether.[15]

Since cyclic oligomers are the exclusive products at equilibrium, high polymers are formed only when the reaction takes place under kinetic control. The yields of high polymer obtained in the condensation depend upon the substituent groups on silicon and the exact reaction conditions, and can be quite low. The oligomeric fraction, consisting mostly of cyclic polysilanes that cannot be converted to polymer, often makes up more than 50% of the products. Some typical yields from the literature are given in Table 5.1. Unfortunately no general best procedure can be stated, because the reaction conditions must be optimized for each particular set of substituents. A further problem is that in laboratory syntheses, yields and molecular weights of the polymers are not easily reproducible. Probably, this is because certain reaction variables, such as the purity of the chlorosilanes, the state of subdivision of the sodium, and the addition rate, are rather difficult to control.

Studies of the rates of formation of polysilanes have led to the currently accepted mechanism, outlined in scheme 5.1.[16] In this model the initiation step, thought to be very slow, is the reaction of $RR'SiCl_2$ with sodium to produce the ion pair

Table 5.1 Examples of Polysilane Polymers

	Yield, %	$M_w \times 10^{-3}$	n/m
Polymers			
$(n\text{-prSiMe})_n$	32	64, 13	
$(n\text{-BuSiMe})_n$	34	110, 6	
$(n\text{-HexSiMe})_n$	11	520, 20	
$(\text{cy-HexSiMe})_n$	20	1200, 19	
$(n\text{-C}_{12}\text{H}_{25}\text{SiMe})_n$	8	1350, 9	
$(n\text{-Pr}_2\text{Si})_n$	39	1160, 27	
$(n\text{-Bu}_2\text{Si})_n$	34	110, 6	
$(n\text{-Hex}_2\text{Si})_n$	6	2000, 1.2	
$(\text{PhSiMe})_n$	55	190, 8	
$(p\text{-MeOC}_6\text{H}_4\text{SiMe})_n$	12	13	
$(p\text{-biphenylSiMe})_n$	40	80	
$(\text{PhCH}_2\text{CH}_2\text{SiMe})_n$	35	290, 4.4	
$[(p\text{-}n\text{-BuC}_6\text{H}_4)_2\text{Si}]_n$	6.2	230, 2.1	
$(\text{PhSiMe}_2\text{SiMe})_n$	9	13	
Copolymers			
$(\text{Me}_2\text{Si})_n\ (n\text{-HexSiMe})_n$	57	170, 10	1.52
$(\text{Me}_2\text{Si})_n\ (\text{PhSiMe})_m$	60	900, 70	1.51
$(\text{Me}_2\text{Si})_n\ (\text{cyHexSiMe})_n$	63	150, 8	1.49
$(\text{PhC}_2\text{H}_4\text{SiMe})_n\ (\text{PhSiMe})_n$	18	400, 3	1.0
$(\text{Me}_2\text{Si})_n\ (\text{Ph}_2\text{Si})_m$	70	350, 2	1.13
$(n\text{-HexSiMe})_n\ (\text{Ph}_2\text{Si})_m$	51	360, 3	0.83
$(n\text{-Hex}_2\text{Si})\ (\text{Ph}_2\text{SiMe})$	17	270	0.67

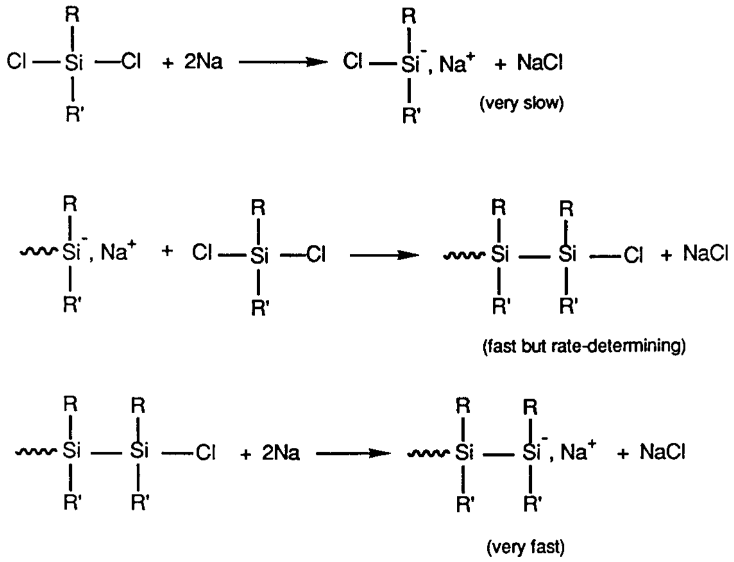
$RR'SiCl^-$, Na^+ (equation (7)). The propagation step (equation (8)), which is rapid but nevertheless rate determining, is the reaction of anion-terminated chains with dichlorosilane to add one silicon unit and produce a chlorine-ended chain. The latter is thought to be reduced rapidly to the anionic form by reaction with sodium. The polysilane chains will alternately be terminated with silyl anions or Si-Cl. This is consistent with evidence from chemical derivatization that both may be present in the products of the reaction.*

$$RR'SiCl_2 + Na \longrightarrow RR'SiCl^-, Na^+ + Cl^- \qquad (7)$$

$$\sim\!\sim RR'Si^- + RR'SiCl_2 \longrightarrow \sim\!\sim RR'Si\text{-}RR'SiCl \qquad (8)$$

The mechanism in Scheme 5.1 can be elaborated further, as shown in Scheme 5.2.[17] The reaction of chlorosilanes with sodium probably proceeds by an initial single electron transfer to form an anion radical, which loses chloride rapidly to form a silyl radical.

*Before isolating the polymer, a reactive monochlorosilane, R_3SiCl, is sometimes added to react with and terminate anionically ended chains. Excess sodium is then discharged by adding a small amount of an alcohol, followed by water. The solution is then washed with water to remove salts, and the organic layer is separated and filtered. Addition of a poor solvent such as ethanol or 2-propanol precipitates the polymer, leaving most of the oligomeric by-product in solution. The separated polymer is heated under vacuum to remove solvent.

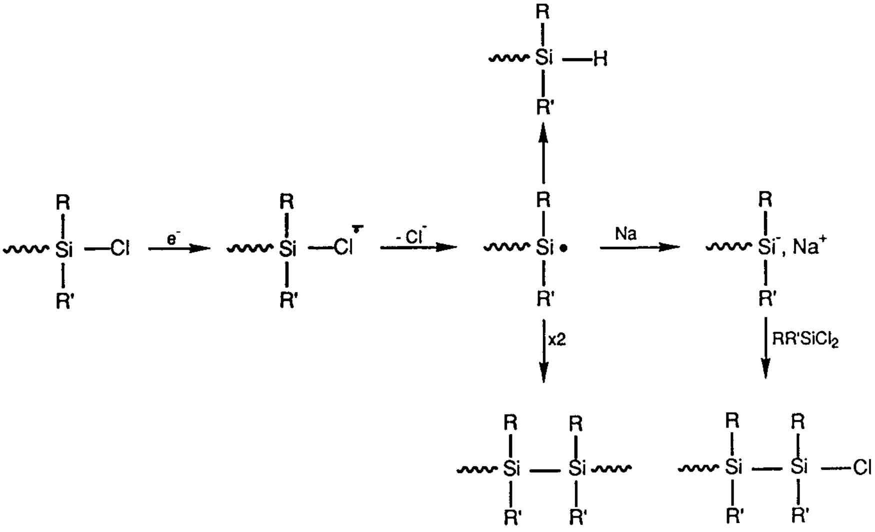


(7a)

(8a)

Scheme 5.1

The facts that Si-H termination is found for some chains[18] and that 5-hexenylphenyldichlorosilane gives mainly cyclized products resulting from addition to the C=C double bond[19] both suggest that radicals are present at some stage. The latter may be reduced in another electron-transfer step to give a silyl anion, bound to the sodium surface. The anion could then react with an Si-Cl bond as in equation (8a) of Scheme 5.1; this is very probably the major reaction leading to chain extension. However, the silyl radical might be directly involved in chain extension by combination with another radical, or could add to a carbon-carbon double bond, or accept a hydrogen atom from the solvent to give an Si-H-terminated chain.



Scheme 5.2

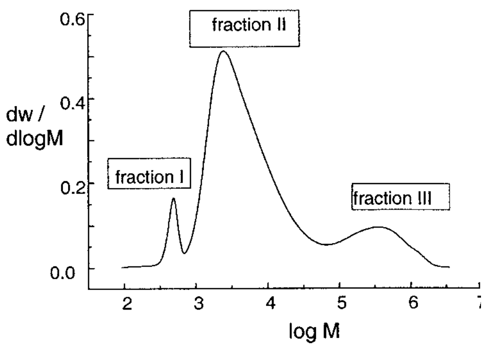
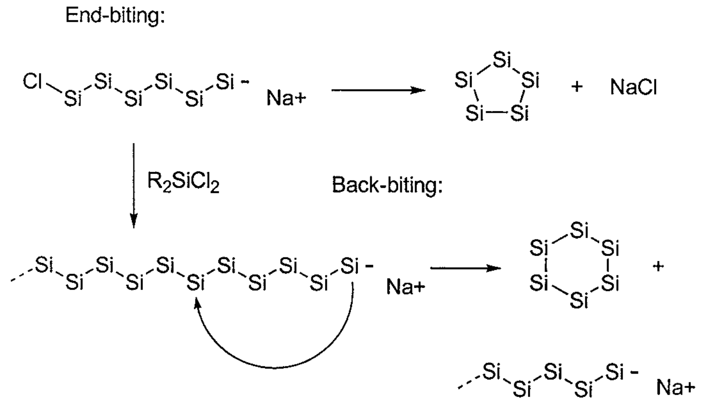


Figure 5.2 Typical molecular weight distribution of $(PhSiMe)_n$, prepared by sodium coupling of $PhMeSiCl_2$. Reprinted with permission from *Organometallics*, 1998, *17*, 59. Copyright 1998 American Chemical Society.

A striking observation is that the molecular-weight distribution of the products from the Wurtz synthesis of polysilanes is usually *trimodal.* An example is shown in Figure 5.2. The very low molecular weight fraction consists of cyclic oligomers, mostly five- and six-membered rings, formed by end-biting or back-biting reactions (equations (9), (10)). The formation of *two* higher molecular weight fractions has been mysterious, but can now be understood following the detailed studies of the Wurtz synthesis of $(PhMeSi)_n$ by Jones and coworkers.[20] This polymer, and polysilanes generally, are now known to adopt helical conformations in solutions, consisting of a mixture of P and M helical segments, separated by chain kinks at which helical reversals take place (see Section 5.7.1).



(9)

(10)

Jones and coworkers propose that the polysilane molecule in its early growth stages forms a single sense helical arrangement, P or M. The stability of the chain increases with its length, because of the increasing electron delocalization as the chain grows longer. But beyond a certain limit, about 35 silicon atoms, further elongation confers no energetic advantage. Eventually a P-M defect will appear, probably initiating from the free end of the chain. The kink can translate along the polymer chain; if it reaches the sodium surface it will provide the conformation needed for a backbiting reaction, leading to a cyclic oligomer and a free polymer molecule. This sequence of events can lead to the intermediate molecular weight fraction.

Another possibility is that two P-M reversal kinks may appear in the same polymer chain. These may translate along the chain to adjacent positions, when both kinks will be mutually annihilated. The annihilation process becomes more likely as the chain becomes longer. Eventually the possibility of backbiting and termination becomes

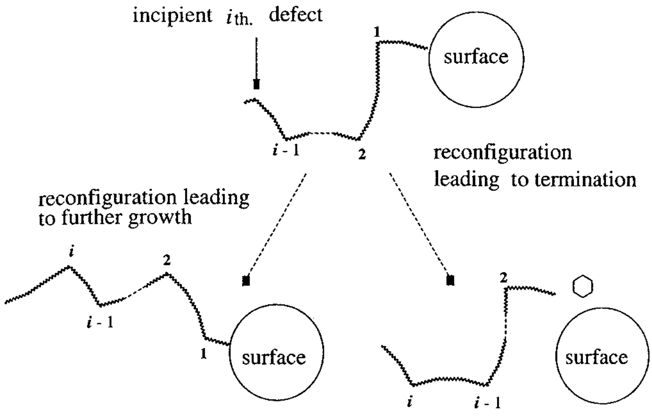


Figure 5.3 Schematic diagram of the progress of polymerization of a polysilane, showing defect-controlled chain growth and termination. Reprinted with permission from reference 20. Copyright 2003 American Chemical Society.

near zero, and the polymer chain can continue to grow in a termination-free process, virtually as a "living polymer." This is believed to lead to the very high molecular weight fraction.

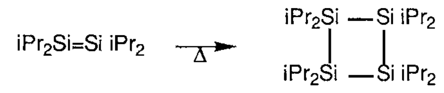
The process is diagrammed schematically in Figure 5.3. A detailed analysis of the kinetics is consistent with the observed bimodal molecular weight distribution for the polymer.[20]

5.3.2 Disilene Polymerization

Polyolefins are, of course, usually synthesized by the catalyzed polymerization of alkenes. Why is an analogous route, polymerization of disilenes, not employed to prepare polysilanes? The reason is paradoxical. The energy barrier to polymerization of doubly bonded silicon compounds is simply too low, so that in most cases they polymerize (or oligomerize) immediately when they are generated!

Photolysis of cyclic silanes or linear trisilanes in hydrocarbon glasses at 77 K leads to divalent silicon species, "silylenes" (equation (11)).[21] When the hydrocarbon is warmed slightly to anneal the glass, the silylenes combine to give disilenes. Upon further warming to melt the hydrocarbon, polymerization of the disilene usually takes place. If the groups R and R′ are moderately large, the product is exclusively a cyclic oligomer. An example is tetra-*iso*-propydisilene, which cyclodimerizes in high yield to the stable four-membered ring (equation (12)).[22]

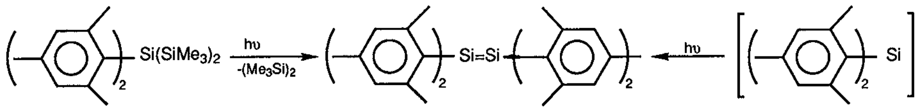
$$\left.\begin{matrix}(RR'Si)_n \\ \text{or} \\ RR'Si(SiMe_3)_2\end{matrix}\right\rangle \xrightarrow[77K]{h\nu} [RR'Si:] \xrightarrow{\Delta} RR'Si{=}SiRR' \xrightarrow{\Delta} (RR'Si)_n \qquad (11)$$



(12)

These reactions illustrate a limitation on the possible structures for polysilane high polymers, no matter how they are prepared. Even when the substituent groups on silicon are small, the cyclic oligomers are thermodynamically more stable than the high polymers.[23] A high polymer may be synthesized in such cases, but only by reactions which do not proceed to equilibrium. As the size of the substituent groups becomes larger, the stability of the polymer becomes so much less than that of its cyclic oligomers that only the latter are formed. Thus polysilanes can be made containing one methyl group and one branched-chain alkyl group, for example (i-PrSiMe)$_n$, but with two branched alkyl groups, the cyclic oligomer is so strongly favored that no polymer is observed, as in the case of (i-Pr_2Si)$_4$.*[22]

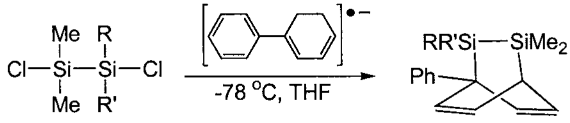
With even larger substituent groups, the disilene becomes the thermodynamically preferred form, and can then be isolated.[24] The best-known example is tetramesityldisilene (**5.5**), ordinarily synthesized as shown in equation (13). The stable, isolable disilenes have an elaborate and beautiful chemistry, but they cannot be polymerized.[25]



5.5 (13)

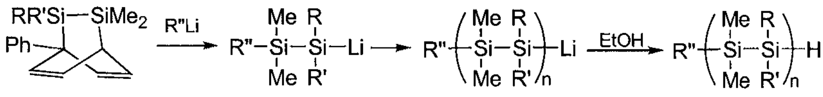
5.3.3 Anionic Polymerization of Masked Disilenes

This valuable new method for synthesis of polysilanes has been pioneered by Sakurai and his coworkers.[26] The "masked disilene" is a biphenyl in which one of the rings is bridged by a disilane group. These molecules can be made by the reaction of biphenyl anion-radical with a dichlorodisilane (equation (14)). The resulting bridged compound reacts with anionic initiators such as n-butyllithium or R_3SiNa compounds cleaving the Si-carbon bonds and producing polymers. Under some conditions, the reaction leads to an anion-terminated, true "living polymer" (equation (15)). The latter can be used to initiate polymerization of other monomers such as methyl methacrylate, to give block copolymers. Quenching the living polymer with ethanol yields a polysilane with H-termination.



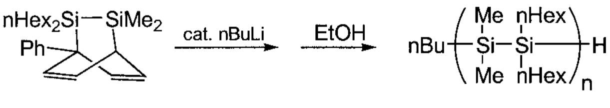
(14)

*Similar, and even more stringent, limitations apply to olefin polymers. In general it is not possible to synthesize polyolefins with more than two alkyl substituents per two carbon atoms. With heavier substitution the polymer becomes unstable relative to the monomer.

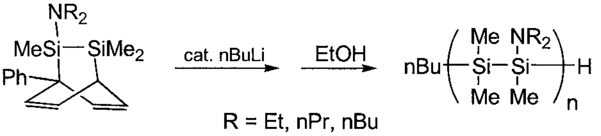


(15)

A remarkable feature of this synthesis is that it provides a route to highly regioselective polysilanes. For example, bridged biphenyl **5.6** reacts with *n*-BuLi to give an exactly alternating polymer, **5.7**. Similarly the dialkyamino substituted bridged biphenyl **5.8** yields the regiospecific polymer **5.9** (equations (16), (17)).[27]



5.6 **5.7** (16)



5.8 **5.9** (17)

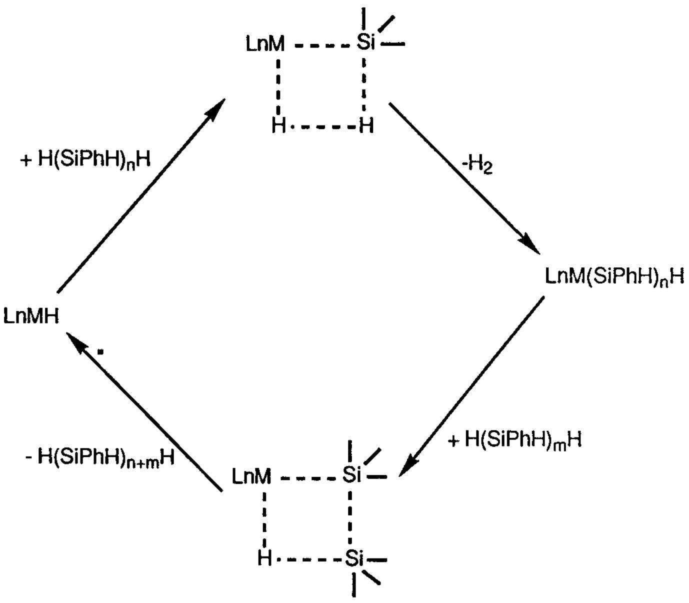
5.3.4 Dehydrogenative Coupling of Silanes

As an alternative route for the synthesis of polysilanes, dehydrogenation of diorganosilanes is attractive (equation (18)). This method might be more easily controlled than the usual alkali metal condensation of dichlorosilanes, especially if the dehydrogenation could be brought about catalytically. A key discovery, by Harrod and his coworkers,[28,29] was that phenylsilane is converted rapidly and quantitatively to an oligomer when it is treated at room temperature with dimethylmetallocenes, $Cp_2M(CH_3)_2$ (M = Ti or Zr, Cp = cyclopentadienyl). The chain length was about 10 silicons for Ti, and 20 for the Zr catalyst.

$$n\ RR'SiH_2 \xrightarrow{\text{catalyst}} H(SiRR')_nH + (n-1)H_2 \qquad (18)$$

Since these early discoveries a great deal of effort has been devoted to improving the catalyst systems. Catalysts based on Ti, Zr, and Hf, with many different ligands, seem to be the most effective, but Pt, Ni, V, Th and U complexes and lanthanide compounds have also been employed.[30] A particularly good result was obtained with the catalyst $(CpCp^*ZrH_2)_2$ (Cp* = pentamethylcyclopentadienyl), which converted $PhSiH_3$ to a polymer with a degree of polymerization of about 130.[31] The mechanism of the catalyzed dehydrocoupling has been controversial, but, at least for the group IV based catalysts, a sigma-bond metathesis mechanism is now accepted (Scheme 5.3).[32]

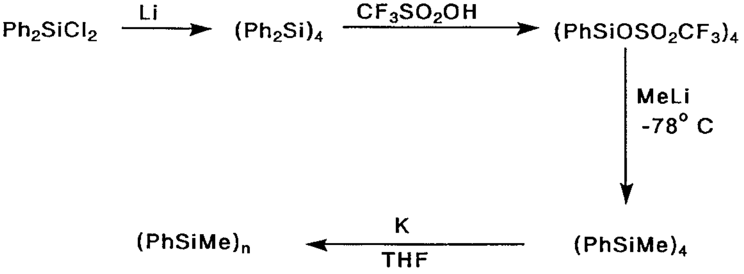
As a method for synthesis of polysilanes, dehydrogenative coupling of silanes is rather limited. Polymers of reasonable molecular weight are obtained only from monoarylsilanes, $ArSiH_3$. Monoalkylsilanes yield only short-chain oligomers, and diorganosilanes, R_2SiH_2, are generally coupled only to the dimer, RSiH-SiHR. These limitations will need to be overcome if this pathway is to become a useful polysilane synthesis.



Scheme 5.3

5.3.5 Other Polymerization Reactions

As explained in Section 4, silicone polymers are usually made by ring-opening polymerization of cyclosiloxane rings. However, because polysilane polymers are unstable relative to cyclosilane rings, ring-opening polymerization cannot generally be carried out. There remains the possibility that strained cyclosilane rings may be used in ring-opening polymerization under kinetically controlled conditions. In fact, the cyclotetrasilane $(Me_2Si)_4$ is observed to polymerize to $(Me_2Si)_n$ on long standing. Poly(phenylmethyl)silylene has been synthesized by ring-opening polymerization of the strained cyclosilane $(PhMeSi)_4$, prepared as shown in Scheme 5.4.[33] Even the slightly strained five-membered ring Si_5Me_9Ph undergoes polymerization to a PhMeSi-Me_2Si copolymer under anionic conditions.[27] Probably other polysilanes could be made by similar polymerization of strained cyclosilanes. The problem with this method is that the synthesis of the required strained cyclosilanes is usually quite difficult. An exception is the four-membered ring compound $(SiCl_2)_4$, easily made from $(Ph_2Si)_4$,



Scheme 5.4

which undergoes ring opening to poly(dichlorosilylene), $(SiCl_2)_n$.[34] The chlorines can be replaced with alkoxy or dialkylamino groups to give fully functionalized polysilanes.[35]

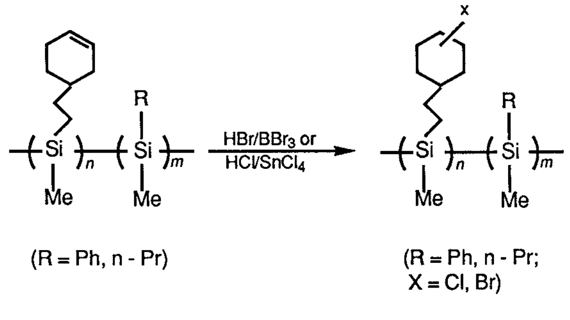
As an alternative to condensation of dichlorosilanes by alkali metals, it is possible to synthesize polysilanes by the reaction of preformed dilithio compounds with dichlorosilanes. An early synthesis of a copolymer by this route is illustrated in equation (19).[10] (see also Section 5.9.2). Finally, poly(phenylmethylsilylene) has been made by thermal decomposition of a silyl-mercury polymer[36] (equation (20)).

$$Li(Ph_2Si)_5Li + Cl(Me_2Si)_5Cl \longrightarrow (Ph_2Si)_n(Me_2Si)_m \qquad (19)$$

$$PhMeSiH_2 + t\text{-}Bu_2Hg \xrightarrow[-2t\text{-}BuH]{} \text{"PhMeSiHg"} \xrightarrow{\Delta} (PhMeSi)_n \qquad (20)$$

5.4 Chemical Modification of Polysilanes

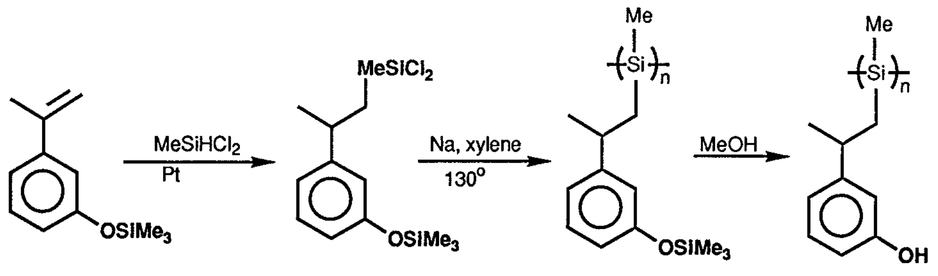
For polysilanes made by Wurtz reaction, the presence of functional groups in polysilane polymers is limited by the vigorous conditions of the sodium condensation reaction. Any substituents that react with molten sodium metal must therefore be introduced after the polymer is synthesized. Halogen atoms can be introduced into alkenylpolysilanes by HBr or HCl addition reactions, as shown for the 3-cyclohexenyl-ethyl polymers in equation (21).[37] Chlorine atoms have also been introduced into arylpolysilanes by chloromethylation, in which $-CH_2Cl$ groups are substituted onto phenyl rings in the polymer.[38]



(21)

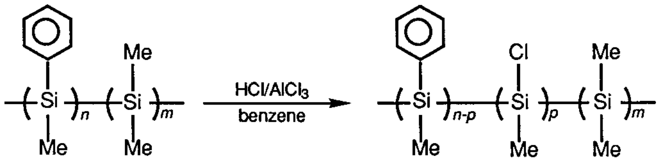
Another approach to functionalized polysilanes is to use protected functional groups. This method was employed to synthesize polysilanes bearing phenolic -OH groups, providing an alkali-soluble polysilane (Scheme 5.5).[39] The protected OH group was introduced as a trimethylsiloxy substituent, which was not affected by the sodium metal during the condensation. Methanol solvolysis later converted the siloxy substituent to the free phenol. Because the polymer is alkali soluble, it can be used as a photoresist which is developed with aqueous solutions (see Section 5.3.2). The phenol function can be further converted to an ester group by reacting it with an acid chloride or to a carboxylic acid by treating it with a diacid chloride followed by hydrolysis.[40]

Polysilanes have also been modified by removal of aryl groups under acidic conditions, to give Si-functional polymers. Phenyl or other aryl groups on silicon can be selectively replaced by halogens, upon treatment with a hydrogen halide and a Lewis acid.



Scheme 5.5

This reaction has been employed with phenyl-containing polysilanes to replace phenyl groups by chlorine (equation (22)).[41] A more versatile substituted polysilane is obtained when trifluoromethanesulfonic (triflic) acid, CF_3SO_3H, is used to replace phenyl substituents.[42,43] Treatment of $(PhMeSi)_n$ with triflic acid in dichloromethane leads to rapid replacement of up to 80% of the phenyl groups by triflate. Some cleavage of Si-Si bonds and consequent degradation of the polymer takes place at high levels of substitution, but the molecular weight is apparently little changed by replacement of up to 50% of the phenyl groups. *p*-Methoxyphenyl substituents are replaced even more rapidly than phenyl. The triflate groups on silicon are highly reactive and can be replaced, for example, by reaction with alcohols, to give methoxy, ethoxy or *t*-butoxy-substituted polysilanes. The triflated polymer catalyzes cationic polymerization of tetrahydrofuran, leading to comblike graft copolymers with a polysilane backbone and polytetrahydrofuran side chains. Likewise, reaction of the triflate containing polysilane with methyl methacrylate forms a comb-like copolymer by group transfer polymerization. Other similar copolymerization reactions should be possible.



(22)

Polyphenylsilane, $(PhSiH)_n$, can be derivatized by free-radical hydrosilylation in the presence of a radical initiator. Alkenes, ketones and aldehydes react readily, to replace up to 93% of the Si-H bonds. This route can be employed to make polysilanes with hydrophilic groups, such as hydroxy, amino and carboxylic acid functions.[43] Dialkylamino substituted polysilanes, made by the anionic polymerization of masked disilenes (see equation (17)), when treated with acetyl chloride give chloro-substituted polysilanes. The chlorine can then be displaced by other nucleophiles.[27]

5.5 Physical Properties of Polysilanes

The properties of polysilanes depend very much on the nature of the organic groups bound to silicon. Some polymers are so highly crystalline as to be insoluble and

infusible. These include the $(Me_2Si)_n$ originally prepared by Burkhard, $(MeEtSi)_n$ and $(Et_2Si)_n$, as well as $(Ph_2Si)_n$ and most poly(diarylsilylene)s.* Decreasing the symmetry reduces the crystallinity and leads to the formation of tractable polymers. Thus $(PhMeSi)_n$ and most poly(arylalkylsilylene)s are resinous solids which melt when heated and are soluble in organic solvents.

Crystallinity is also reduced as the alkyl chains become longer, leading to soluble polymers. The higher poly(methyl-alkylsilylene)s, $(MeSiR)_n$ where R is *n*-propyl or larger, are all soluble, meltable solids. Within this family the glass-transition temperatures decrease to a minimum at R = *n*-hexyl, which has T_g –75 °C. Polymers with R = *n*-butyl to *n*-dodecyl are all rubbery elastomers at room temperature. The symmetrical dialkylsilylene polymers, $(R_2Si)_n$ where R is *n*-propyl or larger, are also soluble solids. Many of these polymers have been carefully studied in the solid state and show interesting phase transitions which will be described further in Section 5.7.2.

Crystallinity is also less for copolymers than for homopolymers that contain similar side groups. For example, copolymer $(Me_2Si)_n(Ph_2Si)_m$ is soluble and meltable, although the corresponding homopolymers are not.[45] Among the polysilane copolymers, the $(PhMeSi)_n$ $(Me_2Si)_m$ ("polysilastyrene") copolymer family has been studied in greatest detail. X-ray powder patterns for polymers with different copolymer compositions show that the crystallinity is at a minimum near a PhMeSi : Me_2Si ratio of 1.

A crucially important property of all polymers is, of course, their molecular weight distribution, usually estimated by gel permeation chromatography (GPC). As mentioned earlier, polysilanes prepared by the usual route, sodium condensation of dichlorosilanes, are commonly found to have bimodal, or even trimodal, molecular weight distributions. If necessary, the high and low molecular weight polymers may be separated fairly well by fractional precipitation. In a typical procedure the polymer is dissolved in a good solvent like THF or toluene, and is precipitated by the slow addition of a poor solvent such as 2-propanol. The material with higher molecular weight is less soluble and precipitates first.

Accurate molecular weight determinations have been obtained for some polysilanes by light scattering,[46,47] but because this technique is much more time consuming than GPC, the results are rather limited. Data from light scattering experiments are shown in Table 5.2, compared with estimated molecular weights from the GPC experiment. The molecular weights determined by light scattering are higher than the GPC values, by factors which depend on the particular structure of the polysilane.

The light-scattering behavior of those polysilanes studied indicates that they are slightly extended and stiffened compared with typical polyolefins. One measure of chain flexibility is the characteristic ratio C, which is also shown in the table. The values of C for most polysilanes of about 20 are larger than those for typical hydrocarbon polymers (~10), indicating that the polysilanes are somewhat less flexible than polyolefins. However, poly(diarylsilylene)s are much more rod-like and inflexible, with persistence lengths greater than 100.[46]

*Soluble poly(diarylsilylene)s can be prepared by attaching long-chain alkyl groups to the aromatic rings, as in $[(p\text{-}n\text{-hexylphenyl})_2Si]_n$.[44]

Table 5.2 Properties of Polysilanes from Light-Scattering Studies

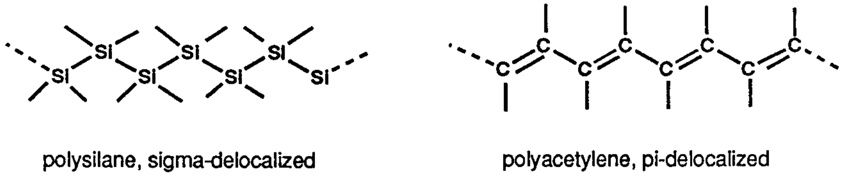
Polymer	Solvent	M_w^{LS}	M_w^{GPC}	M_w/M_n	R_G, nm	C_∞
$(n\text{-PrSiMe})_n$	THF	210,000	180,000	3.1	31	19
$(\text{cyclo-HexSiMe})_n$	$c\text{-}C_6H_{12}$	2,540,000	500,000	2.7	76	14
$(n\text{-Hex}_2\text{Si})_n$	Hexane	6,100,000	1,900,000	2.3	108	21
$(n\text{-Hex}_2\text{Si})_n$	THF	6,300,000	1,900,000	2.3	92	20
$(n\text{-Oct}_2\text{Si})_n$	THF	320,000	2,600,000	2.4	100	30
$(\text{PhSiMe})_n$	THF	46,000	19,000	4.2	21	64
$[(p\text{-}n\text{-BuC}_6H_4)_2\text{Si}]_n$	THF	450,000	500,000	–	60	70

M_w^{LS}: weight average M from light-scattering measurement.
M_w^{GPC}: weight average M from gel permeation chromatography, relative to polystyrene standards.
R_G: radius of gyration.
C_∞: characteristic ratio.

5.6 Electronic Properties of Polysilanes

5.6.1 Electron Delocalization

As explained in the introduction, the polysilanes (and related polygermanes and polystannanes) are different from all other high polymers, in that they exhibit sigma-electron delocalization. This phenomenon leads to special physical properties: strong electronic absorption, conductivity, photoconductivity, photosensitivity, and so on, which are crucial for many of the technological applications of polysilanes. Other polymers, such as polyacetylene and polythiophene, display electron delocalization, but in these materials the delocalization involves pi-electrons.



In most polymers, organic or inorganic, delocalization of sigma-electrons is not evident. Yet we know from modern chemical bonding theory that all electrons can be regarded as delocalized. Why is delocalization in the sigma-electron system not observed, say, for polyethylene? Part of the reason has to do with the ionization energies for the sigma-electrons. For many covalent bonds (C-C, C-H, C-O, Si-O, etc.), the ionization potentials of the sigma electrons are high. Because the sigma-electrons are tightly held, it ordinarily makes little difference whether they are considered to be delocalized or not, and a model assuming localized sigma electrons may be used. But for electrons in Si-Si sigma bonds, the ionization energies are much lower, indeed often less than those of pi electrons in olefins. For example, compare the first ionization potentials for $CH_3CH_2CH_2CH_3$, 10.6 eV; $H_2C{=}CH{-}CH{=}CH_2$, 9.1 eV; and $Me(SiMe_2)_4Me$, 8.0 eV.[48] Because the sigma-electrons in polysilanes are so loosely bound, a localized model is no longer appropriate.[49]

It is also important that the interaction between adjacent silicon orbitals is relatively large. It is convenient to think about this interaction as taking place between neighboring Si-Si bonds, leading to an energy splitting.[48] Corresponding to the filled Si-Si σ bonding orbitals there are Si-Si σ^* antibonding orbitals, which are also split by σ-resonance. As the number of silicon atoms increases, the energy gap between the σ HOMO and σ^* LUMO becomes smaller. Eventually, the set of interacting filled orbitals combine to form a valence band, while the unfilled orbitals combine to generate an empty conduction band (Figure 5.4).

When polysilanes absorb energy in the ultraviolet region, electrons are promoted from the σ valence band to the σ^* conduction band.[50] Absorption maxima for polysilanes fall between about 290 and 410 nm; typical ultraviolet spectra for some polysilanes in solution are shown in Figure 5.5. Because this σ-σ^* transition is "permitted," the electronic absorptions are intense, with extinction coefficients ε between 5,000 and 10,000 per Si-Si bond. Consistent with the splitting portrayed in Figure 5.4, as the number of silicon atoms increases, the energy of the electronic transition decreases. The absorption wavelength therefore increases and eventually reaches a limit when

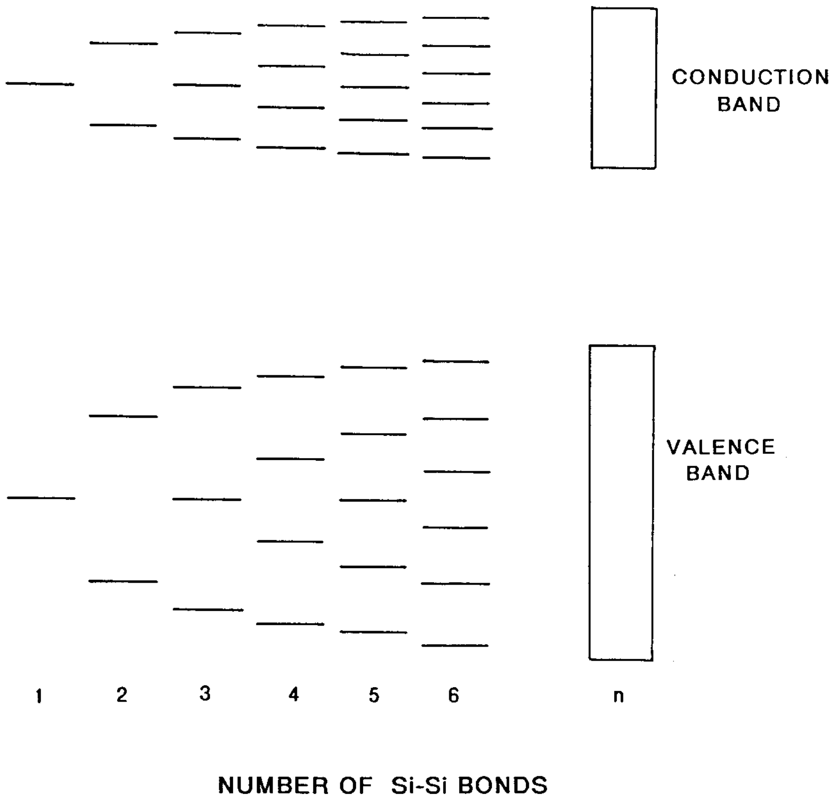


Figure 5.4 Schematic diagram showing splitting of filled and unfilled energy levels for a polysilane as the length of the chain increases, leading to formation of a valence band and a conduction band.

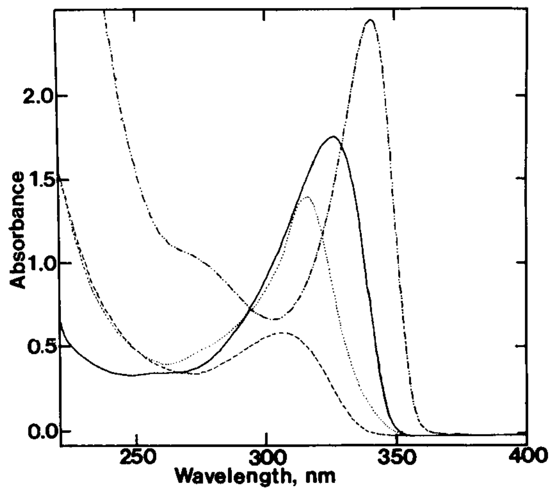


Figure 5.5 Ultraviolet absorption spectra of some polysilanes. -··-·· $(PhSiMe)_n$, ______ $(cyclo\text{-}HexSiMe)_n$, ...(n-HexSiMe$)_n$, ----- (n-DodecylSiMe$)_n$. Reprinted by permission from R. West, *J. Organometal. Chem.*, 1986, *300*, 327. Copyright 1986.

the number of silicon atoms reaches ~30,[51,52] as shown in Figure 5.6. However, the σ-σ^* separation depends on the conformation of the polysilane chain, and therefore the absorption wavelength λ_{max} also depends strongly on the spatial arrangement of the chain. Theoretical[53,54] as well as experimental evidence indicates that λ_{max} increases as the polysilane chain becomes more extended and rodlike.[52,55] Twisting the polysilane chain away from the fully extended conformation leads to successively higher σ-σ^* energies, shifting the absorption to shorter wavelength.

For poly(di-n-alkylsilylene)s in solution at ordinary temperatures, the limiting value of λ_{max} is 305–315 nm. For polysilanes that contain branched alkyl groups, λ_{max} shifts to longer wavelength, for example λ_{max} = 326 nm for (cyclohexyl-SiMe$)_n$, probably because steric repulsions between the substituent groups extend the polymer chain. Arylmethylpolysilanes, (ArSiMe), absorb between 325 and 350 nm, depending on the nature of the aryl substituent. This long-wavelength shift probably results mainly from interactions between the aryl π and polysilane σ electrons, as has been observed for aryldisilanes, but conformational effects may also play a part. Most diarylpolysilanes show λ_{max} near 400 nm, attributed to a rodlike polymer conformation as well as π-σ interactions.

Many polysilanes, both in the solid state and in solution, display a striking thermochromism—the absorption wavelength depends upon temperature. Before discussing this and the other chromotropic effects of polysilanes, it will be necessary to outline the modern theory of rotational conformations, described in the following section.

5.6.2 A New Theory for Rotational Isomeric States: Polysilanes Lead the Way

This section will describe the recent changes in the theory of rotational conformations, which has undergone a drastic revision in the past few years.[56]

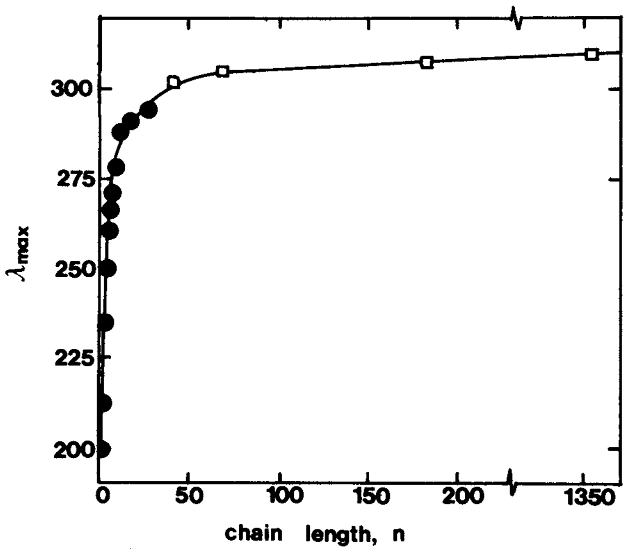


Figure 5.6 Ultraviolet maxima as a function of chain length for alkylpolysilanes. •••••, permethylpolysilanes; □□□□□, (*n*-DodecylSiMe)$_n$. Reprinted by permission from P. Trefonas et al., *J. Polym Sci., Polym. Lett. Ed.* 1983, *21*, 823. Copyright 1983 John Wiley and Sons, Inc.

Every textbook of beginning organic chemistry presents a diagram showing the potential energy diagram for *n*-butane as a function of the rotational angle between the central two carbon atoms. From this, students learn that the stable rotational states of hydrocarbons are *anti* (A),* with a torsional angle $\omega = 180°$, and *gauche* (G), with torsional angle $\omega = 60°$. This model is entirely appropriate for linear hydrocarbons, but it is now clear that these represent a simplified and exceptional case. For polymers other than linear alkanes, rotational isomerism is much more complicated.

Research on polysilane oligomers and polymers has been the major driving force for the paradigm shift to a new model of rotational conformations.[57,58] Until very recently, the structures of polysilanes were mainly described in terms of the older *anti-gauche* model. This is now known to be incorrect, and as a result nearly 20 years of research will probably need to be reinterpreted.

Consider a linear polymer, $(MX_2)_n$. If the substituents X are small compared to the distance M–M between the atoms in the main polymer chain, then the conventional *anti-gauche* model is valid. This is the case for hydrocarbons, and probably for other $(MH_2)_n$ polymers. However, if the van der Waals' radius of the X group becomes a little larger relative to the M–M distance, then repulsions arise between the X atoms on the M atoms in 1,3 positions along the chain. The critical value for such interference is about $R^X/R^{M\text{-}M} = 0.8$. Beyond this value the *anti* conformation is no longer a minimum,

* In much of the earlier literature, the 180° torsional state is denoted as *trans* rather than *anti*. Here we will follow modern practice and use *anti* exclusively to describe this conformation.

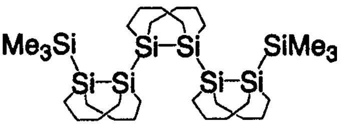


Figure 5.7 Octasilane oligomer with CACAC structure. Reprinted with permission from reference 64. Copyright 2003 American Chemical Society.

but becomes a transition state between two minima with ω ~165°.[59] These conformations are now designated as *transoid*, with the symbol T. Similar interactions between substituents X in the 1,4-positions require a splitting of the G conformation into two states, one with $\omega = 55°$ (*gauche*, G) and one with $\omega = 90°$ (*ortho*, O). This is the situation found for permethylpolysilanes. T and O conformations were first noted in the cyclic silane, $(Me_2Si)_{16}$,[60] and have now been directly observed for Si_4Cl_{10},[61] Si_4Me_{10},[59] and C_4F_{10}.[62]

For still larger substituents X, theoretical calculations show that additional interactions between the side groups arise, and the T and G minima may be replaced by new conformations with torsional angles of ~150° (*deviant*, D) and ~40° (*cisoid*, C).[63] Several polysilanes are known to adopt *deviant* conformations. Examples are $(n\text{-butyl}_2\,Si)_n$ and $(n\text{-pentyl}_2\,Si)_n$, both of which exist in a 7/3 helical arrangement with $\omega = \sim 154°$. *Cisoid* minima are known so far only in constrained polysilanes. An example is the oligomer shown in Figure 5.7, which has the CACAC conformation. Studies of this and similar oligomers also show decisively that σ conjugation does not take place through a Si-Si bond with a small (*cisoid*) dihedral angle.[64]

Figure 5.8 displays a qualitative potential energy diagram for the torsional angles in polysilanes. The barriers between conformations are likely to be small, so intermediate torsional angles may be expected, especially where crystal packing may influence the conformation. For example, although the *anti* conformation is at an energy maximum, it may be favored in the solid state. The one polysilane whose structure is known unequivocally from X-ray crystallography, $(SiCl_2)_n$, in fact has an all-A structure.[34] This may also be the case for $(n\text{-hexyl}_2\,Si)_n$ and perhaps for some modifications of other polysilanes with long n-alkyl side chains (See Section 5.7.2).

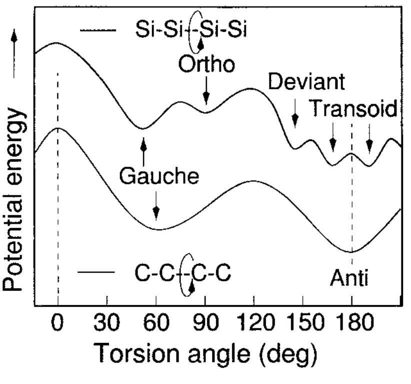


Figure 5.8 Qualitative potential energy diagram for rotation of n-alkanes (below) and polysilanes with side groups C_2H_5 and larger (above). The proposed *cisoid* minimum near 40° is not shown.

5.7 Chromotropism of Polysilanes

The conformation of the polysilane chain, and hence the amount of electron delocalization and the absorption wavelength, may change with temperature, solvent, pressure and so on. The result is that many polysilanes are *chromotropic*.[65] The effect of temperature changes, leading to *thermochromism*, have been most thoroughly investigated.

5.7.1 Thermochromism of Polysilanes in Solution

For many polysilanes in solution, a reversible shift of the σ-σ^* absorption band to longer wavelength takes place when the temperature is decreased. Four types of behavior are found:[65]

1. When polysilane bears two quite dissimilar alkyl groups, the absorption band shifts gradually to longer wavelength as the temperature is lowered. This is the case for $(n\text{-HexSiMe})_n$, shown in Figure 5.9(a).
2. When the two alkyl groups are more nearly similar, as the temperature is decreased the absorption band first shifts gradually, and then narrows and shifts more strongly to longer wavelength. This behavior is shown for $(n\text{-HexSi-}n\text{-Pr})_n$ in Figure 5.9(b).
3. For identical or nearly identical alkyl groups, abrupt thermochromism is seen. The short-wavelength band, typically near 315 nm, disappears and simultaneously a new absorption band grows in near 355 nm. This behavior is found for $(n\text{-Hex}_2\text{Si})_n$ (Figure 5.9(c)). The thermochromic change may take place over a small temperature range of only a few degrees. Near the transition temperature, two different conformations of the polymer must exist in equilibrium.
4. When the substituent groups are large (aryl or branched alkyl) normally no long-wavelength thermochromic shift takes place. This behavior is found for arylalkylpolysilanes, diarylpolysilanes, and $(\text{cyclo-HexSiMe})_n$.

How can this thermochromic behavior be accounted for? Several conflicting explanations have been offered in the past. The situation has recently become clearer as a result of studies by Fujiki and coworkers involving chiral polysilanes.[66] These studies have shown that polysilanes containing chiral side-chain substituents exhibit circular dichroism bands corresponding to their UV absorption, and are therefore helical in solution. This helicity is found even in polymers with a small number (<5%) of chiral substituents. In some cases, for both dialkyl and diarypolysilanes, thermal reversal of the helical screw sense has been demonstrated. For example, poly[(S)-3,7-dimethyloctyl-3-methylbutylsilane] (**5.10**) undergoes a helical reversal at –20 °C in isooctane, where the sign of the CD band (the Cotton effect) changes from positive to negative (Figure 5.10).[67] Similarly, the diarylpolysilane copolymer shown in **5.11** undergoes a reversal of the helical screw pitch at −10 °C.[68]

In a revealing experiment, Toyoda and Fujiki showed that the UV absorption and emission spectra of $(\text{PhMeSi})_n$ are virtually identical to those of the copolymer, $(\text{PhMeSi})_{0.95n}[\text{PhSiCH}_2\text{C}^*(\text{H})(\text{CH}_3)\text{CH}_2\text{CH}_3]_{0.05n}$. The latter is known to be helical in solution from its CD spectrum. The implication is that $(\text{PhMeSi})_n$, which was for many years described in terms of the *anti-gauche* model, is actually helical in solution also.[69] The evidence which is accumulating now suggests that nearly all polysilanes adopt helical conformations in solution.

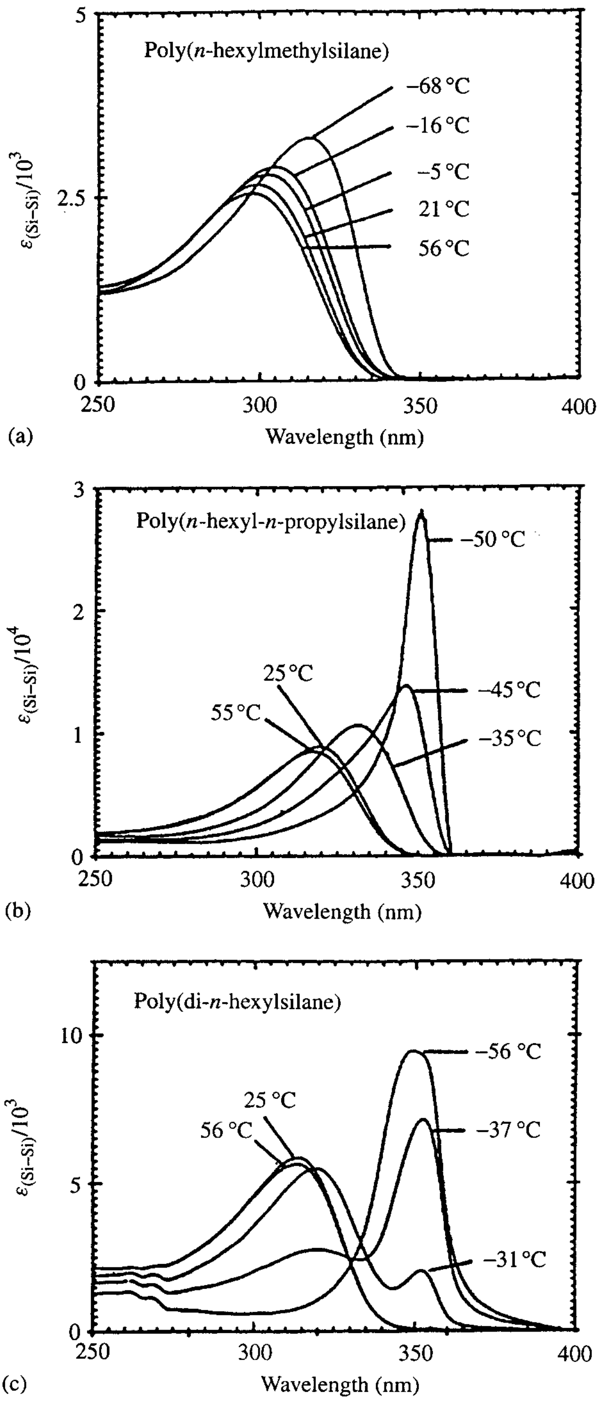
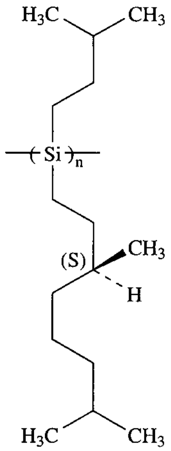
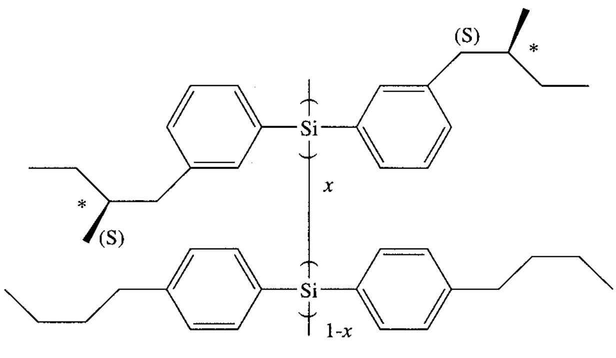


Figure 5.9 UV spectra versus, temperature for three typical polysilanes. (a) $(n\text{-HexSiMe})_n$; (b) $(n\text{-HexSi-}n\text{-Pr})_n$; (c) $(n\text{-Hex}_2\text{Si})_n$. Reprinted with permission from reference 65. Copyright 2001 John Wiley and Sons, Inc.



5.10



$x = 0.2$

5.11

With this new information in mind, an interpretation of the thermochromic behavior of polysilanes in solution can be outlined. We can begin with two calibration points: (1) The polymers $(n\text{-butyl}_2\text{Si})_n$ and $(n\text{-pentyl}_2\text{Si})_n$ absorb at 315 nm both in the solid state and in solution; both polymers as solids are known to have an all-D conformation, with ω~154°. (2) The well-studied polymer $(n\text{-hexyl}_2\ \text{Si})_n$, in its low-temperature phase, absorbs at 375 nm and has a (nearly) all-A conformation. Values of λ_{max} between 315 and 375 nm should correspond to intermediate values of the average torsional angle, ω.

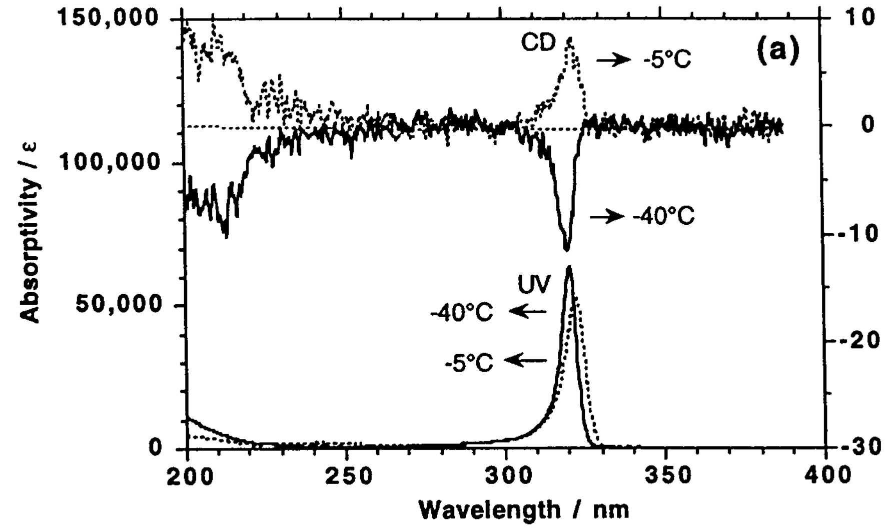


Figure 5.10 UV absorption and circular dichroism spectra of compound **5.10** at −40 °C (solid line) and −5 °C (dotted line), showing reversal of helicity. Reprinted with permission from reference 66. Copyright 1996 American Chemical Society.

Type a behavior (Figure 5.9(a)) can be explained as gradual ordering of the polymer upon cooling, into a rather tightly wound helix with ω~155°, approximately *deviant*. In type b and c polymers, the 315 nm form, probably due to D-helices, may undergo a transition to a more open helial arrangement at the transition temperature. The exact conformation is not known, but the intermediate value of 350 nm for the electronic absorption might result from a *transoid* arrangement, with ω ~165°. Transformation from one helical form to another is consistent with the fact that the radius of gyration of the polymers does not change greatly during the thermochromic transition.[70]

5.7.2 Thermochromism and Conformation of Solid Polysilanes

In the solid state, polysilanes present a far more complicated picture than in solution. Many different phases may be possible for a single polymer, and the transformations between them may be slow, so that the conformation and spectroscopic behavior often depends on the thermal history of the sample. In partial compensation, additional techniques for studying the polysilanes become available for the solids, especially X-ray scattering. Nevertheless the conformations and structures of solid polysilanes are not well understood.

At high temperatures many polysilanes are amorphous. At intermediate temperatures, polysilanes often adopt a hexagonal, columnar mesophase structure (hcm), readily identified by its simple X-ray diffraction pattern.[71] Diagrammatic views of the hcm are shown in Figure 5.11. The polymer chains are arranged in parallel columns in a hexagonal lattice, an arrangement resembling that in nematic liquid crystals. Dialkylpolysilanes in which the two alkyl groups are rather different often maintain this mesophase structure over a wide temperature range. An example is $(n\text{-BuSi-}n\text{-Hex})_n$, which adopts this form from –30 to +200 °C. Similar behavior is observed for polysilane copolymers, for example $(n\text{-Pr}_2\text{Si})_n(n\text{-Hex}_2\text{Si})_m$, which exists in a hexagonal mesophase from below 0 °C to about 200 °C. Related nematic-type mesophases have been found for other kinds of polymers, including some polysiloxanes and polyphosphazenes.

If the side chains are similar in length, crystallization usually takes place as the temperature is further decreased. An important observation is that the UV absorption

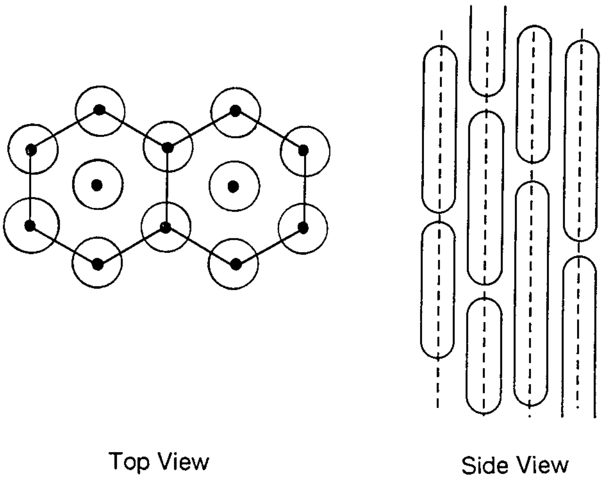


Figure 5.11 Proposed arrangement of polysilane molecules in the hexagonal liquid-crystal mesophase.

bands for the amorphous, hcm and all-D phases, the latter known from X-ray studies of (n-butyl$_2$ Si)$_n$ and (n-pentyl$_2$ Si)$_n$, all have quite similar wavelengths, lying between about 305 and 320 nm. This is also similar to the value found for polysilanes in solution above the transition temperature. It follows that the sigma conjugation must be about equal for all of these forms, and that therefore the average torsional angles are probably similar. In all of these polysilane phases, the rotational conformations are probably mostly *deviant*, with ω~150°.

The solid polysilanes (Me_2Si)$_n$, (Et_2Si)$_n$ and (n-Pr_2Si)$_n$ are all reported to have *anti* conformations, from X-ray studies. Consistent with this assignment, these polymers all show mutual exclusion of infrared and Raman bands, indicating a centrosymmetric unit cell.[72] Theoretical calculations for (Me_2Si)$_n$ indicate that the most stable conformation is *transoid*, but the all-A structure might be forced by crystal packing. However, the UV absorption bands observed for these polymers lie at relatively high energy, 340, 352, and 355 nm, respectively. These wavelengths seem low for all-A polymer chains, making this assignment somewhat doubtful. And in fact the structural studies indicate that small deviations from all-A may be present in (Et_2Si)$_n$ and (n-Pr_2Si)$_n$.[73] At 160 °C the lattice of (Me_2Si)$_n$ transforms from monoclinic to hexagonal, without changing the main chain conformation; a disordering transition then takes place at 220 °C. Disordering transitions occur near 126 °C for (Et_2Si)$_n$ and 235 °C for (n-Pr_2Si)$_n$, probably to a nematic liquid-crystalline form.[74]

As mentioned earlier, the next higher homologs, (n-butyl$_2$ Si)$_n$ and (n-pentyl$_2$ Si)$_n$, adopt an all-D conformation at room temperature, with torsional angles near 154°. Application of pressure, or careful cooling, converts (n-butyl$_2$ Si)$_n$ to a more extended conformation, originally described as *anti* but now known from more detailed X-ray studies to be *transoid.*[75] (n-Pentyl$_2$Si)$_n$ appears to behave similarly. Both polymers undergo transitions to a hcm phase, at 85 °C for (n-butyl$_2$ Si)$_n$ and 56 °C for (n-pentyl$_2$ Si)$_n$.

The next polysilane in the series, (n-hexyl$_2$ Si)$_n$, has been extensively investigated. At room temperature this polymer adopts a conformation which can best be described as *anti*, although recent X-ray studies show that there are slight deviations from $\omega = 180°$, averaging about 5°.[75] Near 43 °C this polymer transforms into a hcm structure. The phase change is accompanied by strong thermochromism, from 375 to 315 nm. (n-hexyl$_2$Si)$_n$ has usually been described in terms of only these structures, but recent studies indicate that other conformations are also possible. Recently this polymer has been found to absorb at 350, 365, or 377 nm, depending on the thermal history of the sample.[76]

The symmetrically substituted polysilanes from (n-octyl$_2$Si)$_n$ to [(n-$C_{14}H_{29}$)$_2$Si]$_n$, can adopt a form absorbing near 350 nm, which was originally assigned to an AG_+AG_- conformation, based mainly on the observation of a four-atom repeat in the crystal structure of the C_{14} polymer.[77,78] This assignment now seems unlikely, since the *gauche* turns would disrupt the conjugation and lead to a much shorter wavelength for the σ-σ^* transition. The actual wavelength suggests conjugation greater than in the all-D but less than in the all-A conformation. More likely conformations with four-atom repeats include AT_+AD_-, AD_+AD_-, $T_+D_+T_-D_-$ and similar variations.[78] The non-crystalline, unsymmetrical polysilanes (n-propylSiMe)$_n$, (n-butylSiMe)$_n$, and (n-hexylSiMe)$_n$ have recently been investigated by X-ray diffraction; the backbone was found to contain a mixture of T, D, and possible O conformations. Crystalline (n-hexylSiMe)$_n$ appears to have a $D_+T_+D_-T_-$ arrangement.[78]

Recent investigations show that multiple crystalline conformations may exist for many polysilanes. An early example was (n-BuSi-n-Hex)$_n$, which adopts a hcm structure at room temperature, with a broad UV absorption at 321 nm. This phase persists on cooling to –23 °C, but further cooling to –25 °C leads to the growth of a new absorption band at 339 nm. If instead the polymer is cooled rapidly from –23 to –28 °C, no 339 nm band appears, but the 321 nm absorption band narrows and shifts to 316 nm. This new phase is assigned to the familiar all-D conformtion. Further cooling to –33 °C or below results in the disappearance of the 316 nm band and growth of an absorption at 349 nm. Thus for (n-Bu-Si-n-Hex)$_n$, in addition to the hcm and *deviant* form, two additional conformations exist with unknown structures.[79] Another good example of multiple conformations obtained on cooling is given by (n-decyl$_2$Si)$_n$. When this polymer is cooled very slowly under near-equilibrium conditions, new absorption bands appear at 375, 365 and 350 nm (Figure 5.12).[79a]

Rapid quenching of polysilanes followed by slow warming can also lead to new conformational states, sometimes in a bewildering array. Here we will consider di-n-decylpolysilane, (n-dec$_2$Si)$_n$.[80] This polymer adopts a hexagonal columnar mesophase at 70 °C, easily identified by its characteristic X-ray pattern (Figure 5.13, i), absorbing at 316 nm (Figure 5.14, i). Rapid chilling to –30 °C produces a new phase with absorption at 355 nm, and some crystallinity in the side chains, as seen from the Figures. Warming just to –25 °C yields a third phase, with an unusual X-ray pattern indicating long-range ordering (Figure 5.13, iii). Simultaneously a new UV band appears at ~380 nm. Upon further warming to –5 °C, the long-range order is lost, and the main UV bands appear at 360 and 375 nm. Next, warming to 20 °C produces yet another phase, with absorptions near 315 and 370 nm and new long-range order. The form of the polymer obtained by casting a film from solution at 20 °C is somewhat different from any of the phases described.

Thus, at least five and perhaps six different phases can be detected for (n-Dec$_2$Si)$_n$. Four of these conformations have UV bands in the 350–380 nm region, perhaps due to mixtures of A, T and D torsional angles. The phase transitions are equally intricate, though quite different, for di-n-octylpolysilane.[80] It is now evident that the solid state

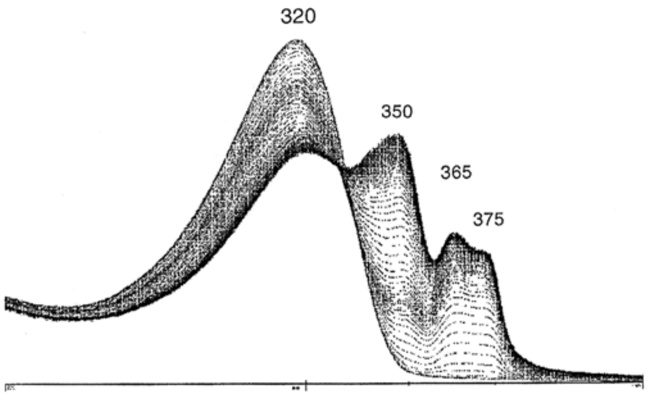


Figure 5.12 UV spectrum of a thin film of (n-decyl$_2$Si)$_n$, cooled slowly from 25 °C to –20 °C, showing development of new absorption bands first at 375 and 365 nm, then at 350 nm.

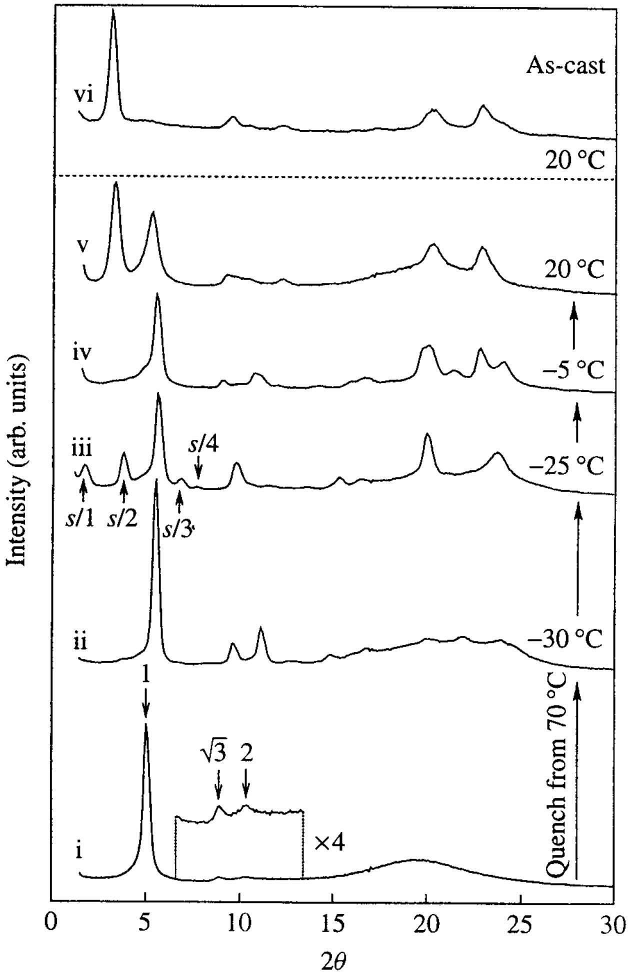


Figure 5.13 X-ray powder patterns for $(n\text{-decyl}_2Si)_n$, at 70 °C (i), quenched rapidly to −30 °C (ii), and then gradually warmed. Five different structural phases are observed. Reprinted with permission from reference 80. Copyright 2000 American Chemical Society.

conformations of polysilanes are much more complicated and perplexing than anticipated. Determination of the conformations and structures of polysilane polymers is likely to occupy investigators for many years.

5.7.3 Other Forms of Chromotropism

Solvatochromism refers to dependence of the electronic absorption on the nature of the solvent. Most polysilanes do not exhibit solvatochromism; for instance, the UV absorption of $(n\text{-hexyl}_2Si)_n$ is not affected by large changes in solvent polarity.[57,81] Polysilanes which contain oxygen atoms in the side chains do however show solvent dependence of the UV transition energy, with the absorption band shifting to longer wavelengths as the solvent polarity increases. An example is shown in Figure 5.15.[82] The polar solvents

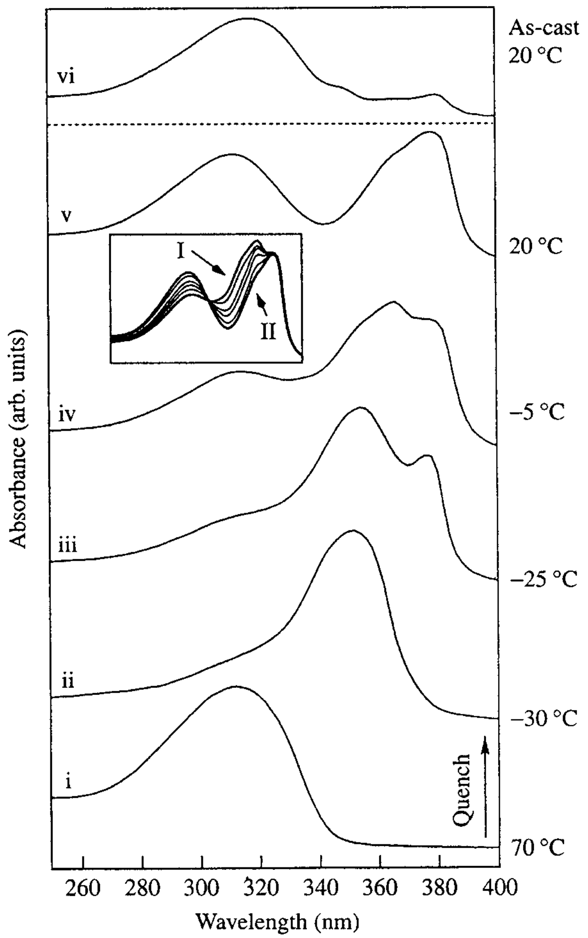


Figure 5.14 UV spectra (n-decyl$_2$Si)$_n$, under the same temperature conditions as in Figure 5.13.

may interact with the oxygen atoms in the side groups, straightening the polymer chain and slightly increasing conjugation. In some cases a small amount of a polar compound can produce dramatic changes in the UV. As shown in Figure 5.16, when $(CF_3)_2CHOH$ is added to a solution of $\{[n\text{-}PrO(CH_2)_4]_2Si\}_n$ in chloroform, the normal UV band at 325 nm suddenly disappears and is replaced by an absorption at 348 nm.[82] In this case the effect is believed to result from strong hydrogen bonding by the fluorinated alcohol to the side-chain oxygens. Unexplained is the fact that the conformational change takes place so abruptly, between 4% and 5% of added alcohol.

Polysilanes with several oxygen atoms in the side chains have been studied by Cleij and coworkers.[83,84] These polysilanes may become water soluble, as is the case for $[MeSi(CH_2)_3(OCH_2CH_2)_3OCH_3]_n$. In THF solution at 20 °C this polymer absorbs at 305 nm, but in water the UV band is shifted to 281 nm. The water may cause tighter coiling of the polymer chains, perhaps due to micelle formation. Between 46 and 70 °C, the water solution undergoes phase separation. The UV band shifts to 320 nm, consistent with partial straightening of the polymer chain after phase transition. These polymers also display ionochromism.

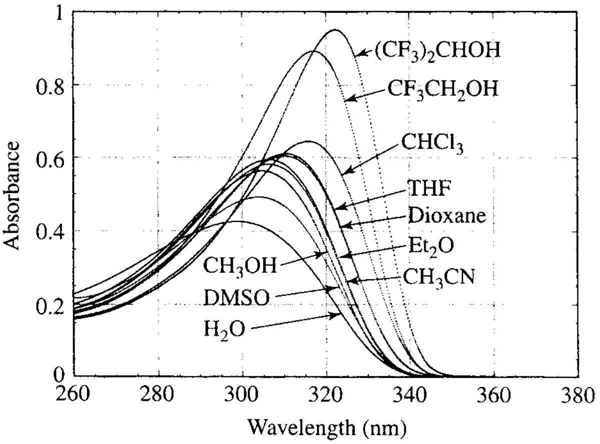


Figure 5.15 UV spectra for $[MeSi(CH_2)_3(OCH_2CH_2)_3OCH_3]_n$ in various solents, showing solvatochromism. Reprinted with permission from reference 65. Copyright 2000 John Wiley and Sons.

Ionochromism refers to dependence of the electronic absorption on the presence of ions. This phenomenon has also been observed mostly for oxygen-containing polysilanes. Generally, the ionic (usually lithium) salts are added to a solution of the polymer that is then cast into a film. An example is $[n\text{-OctSi}(CH_2)_4OCH_2CH_2OC_2H_5]_n$, which normally undergoes a thermochromic transition in the solid state from 320 to 354 nm at –32 °C. Addition of lithium trifluoromethanesulfonate progressively inhibits this transition, and when the salt concentration reaches 50 mol % no thermochromism at all

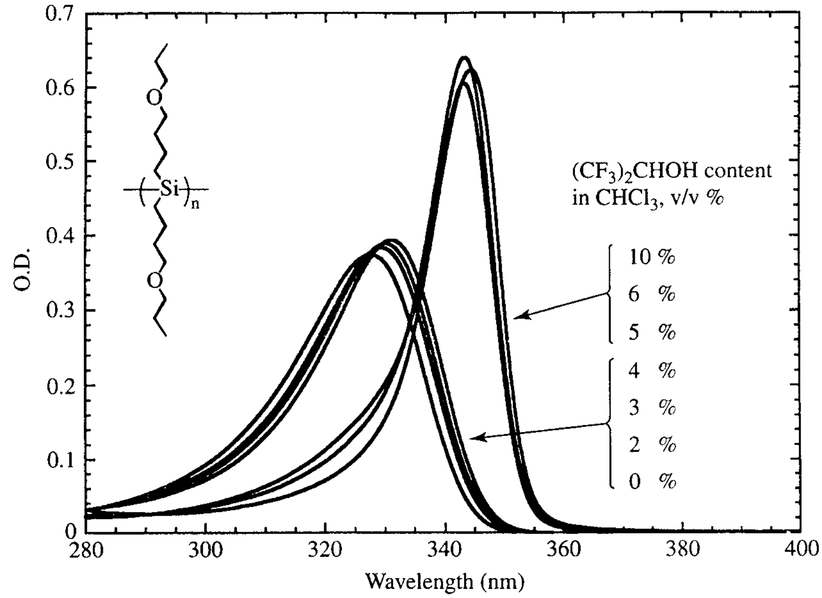


Figure 5.16 UV spectra for $[(n\text{-PrOCH}_2CH_2CH_2CH_2)_2Si]_n$ in $CHCl_3$ upon addition of $(CF_3)_2CHOH$, showing the abrupt solvatochromic shift. Reprinted with permission from reference 82. Copyright 1997 American Chemical Society.

is observed.[85] This effect, in which a chromic change is inhibited, is termed *negative ionochromism.*

Contrasting behavior is observed for the polysilane $\{[C_2H_5OCH_2CH_2O(CH_2)_5]_2Si\}_n$. As shown in Figure 5.17, addition of lithium triflate to a thin film of the polymer promotes the bathochromic shift, increasing the midpoint temperature for the transition from –45 to +50 °C and providing a dramatic example of *positive ionochromism.*[86] This effect is reversible by the addition of water or THF vapor, which returns the polymer to its original state. When the water or THF is removed in vacuum, the long-wavelength absorption is regenerated. Evidently, these effects involve complexing of lithium ions to the oxygens in the side chains of the polymer, but why the ionochromism is negative in some cases and positive in others is not at all understood.

Other types of chromotropic behavior in polysilanes have only begun to be investigated. The transformation of (n-butyl$_2$ Si)$_n$ and (n-pentyl$_2$ Si)$_n$ under pressure from the all-D to a more extended conformation (described in the literature as *anti*, but more likely *transoid*)[75] is an example of *piezochromism.* Other polysilanes might also exhibit piezochromic behavior, and experiments to study this seem warranted.

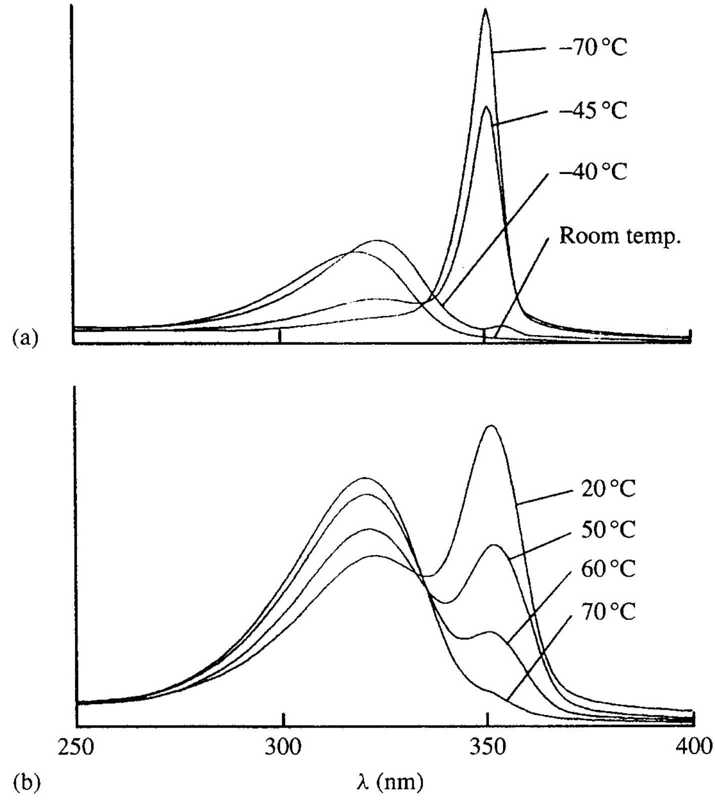


Figure 5.17 UV spectrum versus temperature for a film of $\{[C_2H_5OCH_2CH_2O(CH_2)_5]_2Si\}_n$: (a) neat; (b) with the addition of 75 mol % of $LiSO_3CF_3$, showing a strong positive ionochromic effect.

Mechanical stretching of polymer chains, by drawing or rubbing, can also cause changes in the conformation. For (n-pentyl$_2$ Si)$_n$, the same chromotropic change found under high pressure can also be induced by drawing.[87] A second example is given by (n-HexSiMe)$_n$, which is normally amorphous at room temperature with UV absorption at 300 nm. Drawing of films of this polymer leads to an oriented form absorbing at 338 nm.[88]

Chromotropism in the presence of an electric field, *electrochromism*, has been observed for just one polysilane, the copolymer ($CF_3CH_2CH_2SiMe$)$_n$-*co*-(nPrSiMe)$_m$, $n : m = 45 : 55$.[89] The UV band for this polymer is intensified by 50% and shifted from 294 to 299 nm, in an electric field of 10^8 v/m. The changes are reversible when the field is removed. Other polysilanes with polar side groups might also show electrochromic behavior, but none have been studied.

Magnetic fields may also affect the electronic absorption bands of polysilanes (*magnetochromism*) and this has been investigated in a few polysilanes. For (PhSiMe)$_n$, in a 12 T field the absorption intensity increased by about 15%. When the field was removed a rebound effect was noted, with the intensity decreasing to about 2/3 of it original value.[90] Probably these effects reflect in some way the strong diamagnetism of the phenyl rings.

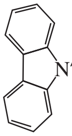
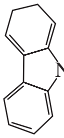
5.8 Electrical Conductivity and Photoconductivity

Polysilane polymers are electrical insulators, with conductivities well below 10^{-10} S cm^{-1}, but addition of oxidizing agents can remove electrons from the delocalized, high energy molecular orbitals, generating vacancies (holes) which can migrate along the chain. Thus the doped polysilanes become one-dimensional semiconductors. This was reported in the 1981 paper which first described sigma-delocalization in polysilanes.[9] Early experiments were done using SbF_5 as the oxidant, but this leads to degradation of the polysilane chain. Cleaner results are obtained with iodine as the oxidant. For several polysilanes conductivities of 10^{-8} to 10^{-6} S cm^{-1} were found (Table 5.3) which could be correlated with the ionization potentials of the polymers (lower ionization potentials leading to higher conductivity). This is consistent with electron transfer from the polymer to iodine, forming I_3^-, and the generation of delocalized holes along the polysilane chain.[91,92]

For polysilanes with nitrogen atoms in the side-chain, as seen in the table, conductivities were much higher, up to 10^{-2} S cm^{-1}. Here, oxidation probably takes place at the nitrogen atoms, followed by delocalization of the positive charges from the nitrogen atoms to the polysilane chain. To demonstrate that the polysilane chain is actually involved in the conduction, a carbazolyl-containing polysiloxane was investigated along with the corresponding polysilane. The conductivity of the polysilane was about 300 times as great as the polysiloxane, showing that the conductivity involves electron migration in the polysilane chain. Oxidation of polysilanes with $FeCl_3$ has also been investigated. $FeCl_3$ produces relatively higher conductivity with polysilanes containing a phenyl group, perhaps due to charge transfer from the aromatic π orbitals to the oxidant. Electrons must hop from one polymer chain to another to account for the bulk conductivity.

Polysilane polymers also show photoconductivity when irradiated with ultraviolet light,[93] and are excellent charge transport materials in electrophotography.[94] In a typical charge transport experiment, electrical charges are generated at the surface of a polysilane film from a photoactive layer such as selenium (Figure 5.18) and moved through

Table 5.3 Conductivities of Polysilanes (S cm^{-1}) Doped with Iodine or $FeCl_3$[a]

	Sidechains	IP (Ev)	Dopant	
			I_2	$FeCl_3$
n-Bu	*n*-Bu	5.83	4×10^{-8}	2×10^{-10}
$PhCH_2$	$PhCH_2$	5.78	4×10^{-7}	8×10^{-7}
n-Oct	*n*-Oct	5.73	4×10^{-7}	1×10^{-7}
Ph	Me	5.42	1×10^{-6}	6×10^{-6}
$Me_2NC_6H_4$-*p*	Me	5.01	1×10^{-3}	4×10^{-4}
$Me_2NC_6H_4(CH_2)_3$	Me	5.56	1×10^{-2}	7×10^{-6}
 N′–$(CH_2)_3$	Me	5.65	1×10^{-3}	2×10^{-5}
 N–$(CH_2)_3$[b]	Me[b]		3.5×10^{-6}	etc.

[a]Data from reference.[91]
[b]Polysiloxane polymer.

the polymer film by an electrical field. Polymers which have been studied include $(PhSiMe)_n$, $(PhSiEt)_n$, polysilastyrene, $(n\text{-octylSiMe})_n$, and $(\text{cyclo-HexSiMe})_n$. All these polysilanes transport charge, and their efficiency is almost independent of the nature of the substituent groups. In each case the conductivity is entirely by hole transport; that is, positive but not negative charges appear to migrate through the polysilane layer under the influence of an electric field. The polysilanes show charge mobilities as high as 5×10^{-3} units, and activation energies for charge transport even lower than those of materials now used in electrophotography (Table 5.4).

As charge transport materials, the polysilanes are unique in that the active sites are on the polymer backbone itself. In other electrophotographic materials, charged sites

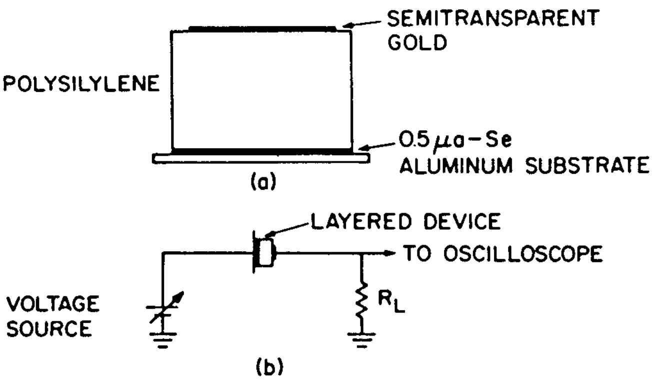


Figure 5.18 Schematic drawing of experiment used to determine hole conductivity of polysilanes. Reprinted by permission from M. Stolka et al., *J. Polym. Sci., Polym. Chem. Ed.*, 1987, *25*, 823. Copyright 1988 John Wiley and Sons, Inc.

Table 5.4 Charge Mobility and Activation Energy for Charge Transport for Electrophotographic Polymers

Polymer	Hole Mobility $cm^2 V^{-1}s^{-1}$	Activation Energy, eV
Polyvinyl carbazole	10^{-8}	0.6
Amine-doped polycarbonate	10^{-4}	0.3–0.7
$(PhSiMe)_n$	$>10^{-4}$	0.28
Amine-doped $(PhSiMe)_n$	10^{-3}	—

are on pendent groups, as in poly(vinyl carbazole), or on molecules mixed with the polymer, as in polycarbonate film doped with aromatic amines. "Doping" of the polysilane with aromatic amines increases the hole mobility by almost another order of magnitude, as shown from the table.

In addition to photoconductivity, polysilanes have been found to exhibit marked non-linear optical properties,[95–97] suggesting that they may eventually be useful in laser and other optical technology. The third-order non-linear susceptibility, χ^3, is a measure of the strength of this effect. The non-linear properties of polysilanes, like the absorption spectra, seem to be dependent on chain conformation and are enhanced for polymers having an extended, near *anti* conformation (Table 5.5). The value of 11×10^{-12} esu observed for $(n\text{-}Hex_2Si)_n$ below its transition temperature is the largest ever observed for a polymer which is transparent in the visible region.

5.9 Luminescence of Polysilanes

5.9.1 Photoluminescence

The fluorescence of polysilanes has received much attention in recent years, in part because of the discovery that some polysilanes are electroluminescent, and so may have applications in display technology. Fluorescence spectra, quantum yields, lifetimes and other properties for dialkylpolysilanes have been thoroughly investigated by Sun and coworkers.[98] Dialkylpolysilanes exhibit fluorescence of a rather normal type, in which the emission is a mirror image of the absorption, with a rather small Stokes shift. This suggests that the emission takes place from a highly delocalized state, probably an

Table 5.5 Third-Order Non-linear Susceptibilities for Polysilanes and Some Related Polymers

Polymer	T °C	x^3, esu × 10^{12}
$(PhSiMe)_n$	23	1.5
	25	7.2, 4.2
$(n\text{-}Hex_2Si)_n$	23	11.0
	50	2.0
$(n\text{-}Hex_2Ge)_n$	–11	6.5
	23	3.3
$(p\text{-}C_6H_4CH{=}CH_2)_n$	25	7.8
Polydiacetylenes, various		1–400

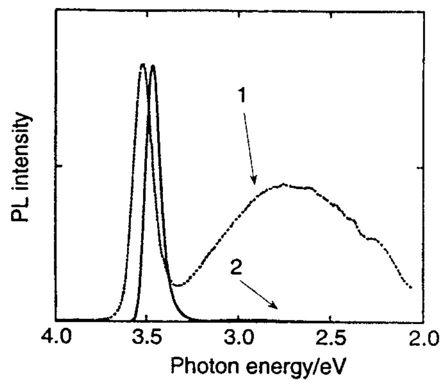


Figure 5.19 Photoluminescence spectrum of $(PhSiMe)_n$ (1) and $(n\text{-pentylSiPh})_n$, at 20 K. The broad low-energy peak for $(PhSiMe)_n$ is due to chain branching. Reprinted with permission from reference 57. Copyright 2000 Kluwer Academic Publishers.

extended *transoid* region. If the excitation takes place in a more localized part of the polymer chain, it must be rapidly transferred to a delocalized region.

Among aryl-alkylpolysilanes, $(PhMeSi)_n$ has received the greatest attention. Typical samples of this polymer show a sharp, weakly shifted emission band like those for the dialkylpolysilanes, and in addition a broad absorption with a much greater Stokes shift to the visible region, shown in Figure 5.19. The origin of this visible emission was controversial but has now been shown to arise from defects in the backbone structure, evidently branch points resulting from some $PhSiCl_3$ being present in the $PhMeSiCl_2$ starting material.[99] When $(PhMeSi)_n$ is made from carefully purified $PhMeSiCl_2$, it does not show visible fluorescence. The same is true for the polymer $(n\text{-pentylSiPh})_n$, prepared from a pure dichlorosilane (Figure 5.18).[100]

The deliberate introduction of branch points in the structure of dialkylpolysilanes also leads to a broad long-wavelength emission, which appears to be characteristic for three-dimensional polysilanes.

5.9.2 Electroluminescence

The discovery that polysilanes show luminescence in an electric field, electroluminescence, has aroused considerable interest in the possible use of polysilanes in light-emitting diodes and other electronic devices.[101,102]

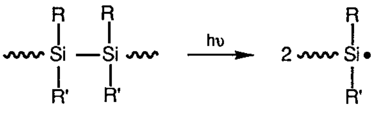
Dialkylpolysilanes and $(PhMeSi)_n$ display rather weak emission, $\sim 10^{-4}$ % photons/electron, in the near ultraviolet region, 340–370 nm. Diarylpolysilanes appear to be much more promising. Among these, poly[di(*p*-*n*-butylphenyl)]silane has been the most thoroughly studied. It produces blue light at the edge of the UV region, at 407 nm, with an efficiency of ~0.1% photon/electron.[103] Polysilole polymers (**5.11**) also show relatively high efficiencies.[104] Various copolymers of polysilanes with other conjugated polymers also show promising electroluminescent properties.[105] Much more work in this area is likely to appear in the future.

5.10 Photodegradation of Polysilanes

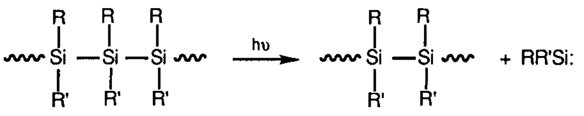
When irradiated with ultraviolet light, most polysilanes undergo chain scission into smaller fragments. When polysilanes $(RR'Si)_n$ are photolyzed with UV light ($\lambda = 254$ nm)

in the presence of triethylsilane, large amounts of $Et_3SiSiRR'H$ are produced. This product arises from the insertion of silylene into the Si-H bond of triethylsilane, as shown in equation (23). Upon exhaustive photolysis the other major product is the disilane, HSiRR′SiRR′H. From these and other experiments it appears that the major reactions in photolysis of polysilanes are homolysis to give silyl radicals (equation (24)) and silylene elimination (equation (25)).[106,107] Some chain scission with transfer of a substituent also takes place (equation (26)).[108] Chain shortening results from all of these reactions, but especially from equations (24) and (25). When 254 nm UV light is used, photolysis ceases at the disilane stage because UV radiation is no longer absorbed. Secondary reactions also occur, leading in the case of $(n\text{-}Hex_2Si)_n$, to the formation of Si-H bonds and Si=C double bonds. There is also evidence for the formation of persistent silyl radicals of the type -SiRR′-SiR-SiRR′-. Photolysis ceases at the disilene stage where the UV light is no longer absorbed. With UV photons of lower energy ($\lambda > 300$ nm), elimination of silylene (equation (24)) does not take place, and the major initial step is homolytic scission.[107]

$$Et_3Si\text{-}H + RR'Si: \longrightarrow Et_3Si\text{-}SiRR'\text{-}H \tag{23}$$



(24)



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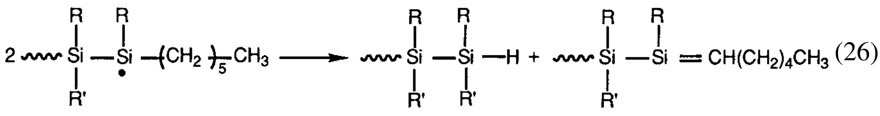


(26)

When aryl substituent groups are present, more complex photolytic reactions occur, and some cross-linking takes place as well as chain scission. Groups containing C=C double bonds are even more effective at bringing about cross-linking. This leads directly to the topic of cross-linking in polysilanes.

5.11 Cross-Linking

For some uses it is important to form bonds that link different polysilane chains, to transform soluble, meltable polysilanes into insoluble resins. This process is vital if the polysilanes are to be used as precursors to silicon carbide ceramics, since, if cross-linking is not carried out, most of the polymer is volatilized before thermolysis to silicon carbide can take place. Several methods have therefore been developed to bring about cross-linking of polysilanes.[109,110]

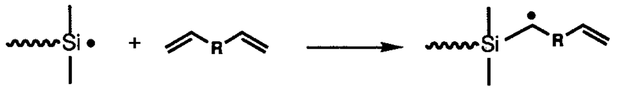
5.11.1 Photolysis of Alkenyl-Substituted Polysilanes

As mentioned in the preceding section, when vinyl or other alkenyl groups are present as substituents, photolysis leads to cross-linking, which dominates over chain scission. Probably the cross-linking results when silyl radicals formed in the initial photolysis add to vinyl carbon atoms on neighboring chains, but other mechanisms are also possible.

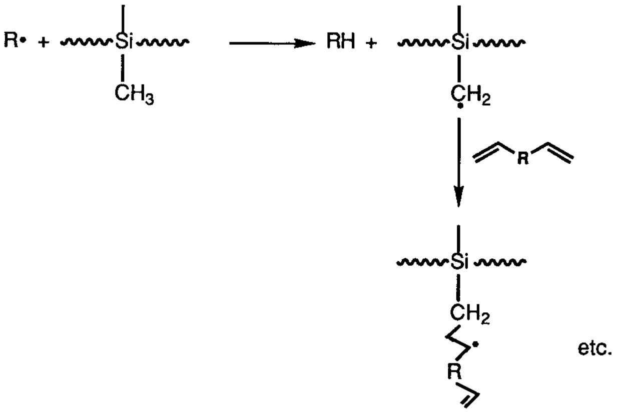
5.11.2 Free-Radical Cross-Linking with Polyunsaturated Additives

The same reactions can occur when the C=C double bonds are present on a molecule which is simply mixed with the polysilane and can then serve as a cross-linking agent. This provides a very general method for cross-linking of any polysilane. The radicals necessary to cause cross-linking can be formed by photolysis of the polysilane or by heating the mixture with a free radical initiator such as azobis(isobutyronitrile), AIBN. To be useful as cross-linking agents, additive molecules must include two or more unsaturated groups. Compounds which have been used include tetravinylsilane; trivinylphenylsilane; the hexavinyldisilyl compounds $(CH2{=}CH)_3Si(CH2)_nSi(CH{=}CH)_3$, $n = 2$, 4, or 6; 1,5-hexadiene; and triallylbenzene-1, 3,5-tricarboxylate.

In photochemical cross-linking, the silyl radicals formed in the initial cleavage reaction probably add to the C=C double bonds. This addition produces cross-links and also generates new carbon radicals which may cause further cross-linking reactions (equation (27)). Using thermal radical initiators, the first steps may be either addition of initiator radicals to the double bonds of the polyunsaturated compound, or abstraction of hydrogen from organic groups on the polysilane. For instance, loss of hydrogens from methyl groups on the polysilane would lead to formation of crosslinks (equation (28)).



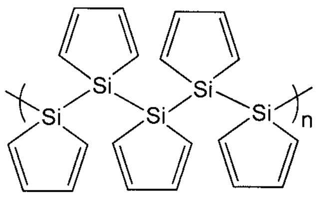
(27)



(28)

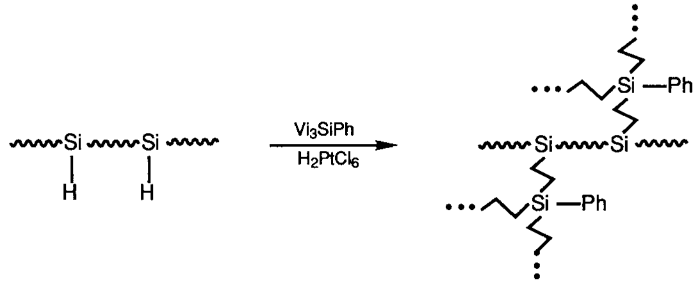
5.11.3 Hydrosilyation Cross-linking

Polysilane copolymers that contain a limited amount of hydrogen can be obtained using the Wurtz synthesis (**5.12**). The isolation must however be carried out carefully under



5.12

neutral conditions so that the Si-H groups are not lost through hydrolysis. These polymers are low-melting solids or in some cases (R = n-hexyl) thick fluids at room temperature. The well-known hydrosilylation reaction is effective for bringing about cross-linking of such polymers. Trivinylphenylsilane was used as the cross-linking agent, in the presence of a trace of chloroplatinic acid as a catalyst (equation (29)), but in practice any compound containing several vinyl groups could be used. The mixture of reactants forms a viscous fluid or paste which sets to a firm rubbery solid as cross-linking takes place. By this process "room-temperature vulcanization" (RTV) of polysilanes can be brought about, analogous to the RTV polymerization of silicone elastomers.



(29)

5.12 Structural Arrangements in Polysilanes

5.12.1 Configurations and Stereochemistry

Polysilane homopolymers in which all the side groups are identical, such as $(n\text{-Bu}_2\text{Si})_n$, exhibit no stereoisomeric effects since a plane of symmetry can be drawn through each silicon atom. In polymers bearing two different substituents on each silicon, for example, $(n\text{-BuSiMe})_n$ each silicon is a stereogenic center, and the relative configurations of other silicon atoms becomes significant. Consider a polysilane with silicon atoms bearing substituents A and B. The relationship between neighboring atoms is *meso* (or M) if they have the same configuration, *racemic* (or R) if they have opposite configurations. In general, polymers which contain stereogenic centers are called isotactic if all the relative configurations are M, syndiotactic if all relative configurations are R, and atactic if the configurations are random.[111]

For a triad of silicon atoms, there are four possibilities: M,M (isotactic), R,R (syndiotactic), and M,R and R,M (heterotactic); the last two are equivalent since the polymer chain may be "read" in either direction. If there is no stereochemical preference, as in an atactic polymer, the amounts of isotactic, syndiotactic, and heterotactic triads would be 1 : 1 : 2, the heterotactic arrangement being twice as probable.

If the relative configuration of two nearest neighbors on each side is considered, there are ten independent arrangements:

RRRR	RMMR
RRRM = MRRR	MRRM
RRMR = RMRR	MMMR = RMMM
RRMM = MMRR	MMRM = MRMM
RMRM = MRMR	MMMM

Various methods may be used to examine configurations of polysilanes, but ^{29}Si NMR spectroscopy has been the most useful. Silicon-29, like carbon-13, has spin 1/2 and a relatively low abundance, 4.7%. Nuclear magnetic resonance (NMR) spectroscopy using ^{29}Si has been important for the characterization of siloxane polymers, and is proving to be equally useful for polysilanes.

The ^{29}Si NMR spectra of solutions of several dialkylpolysilanes is shown in Figure 5.20. For $(n\text{-}Hex_2Si)_n$ where there is no possibility for stereoisomerism, the resonance is a single sharp line showing that all the silicon atoms have identical environments. But for the $(n\text{-alkyl-SiMe})_n$ polymers, which contain stereogenic silicon atoms, multiple resonances appear. The symmetrical, five- to seven-line patterns can be interpreted as arising from completely atactic polymers, having a statistical distribution of relative configurations at the two nearest-neighbor silicon atoms on each side.[112,113]

In arylmethyl polymers the results are quite different. For the best studied example, $(PhSiMe)_n$, the ^{29}Si NMR pattern consists of three broad lines, centered at −39.2, −39.9 and −41.2 ppm, evidently corresponding to different tacticities of atom

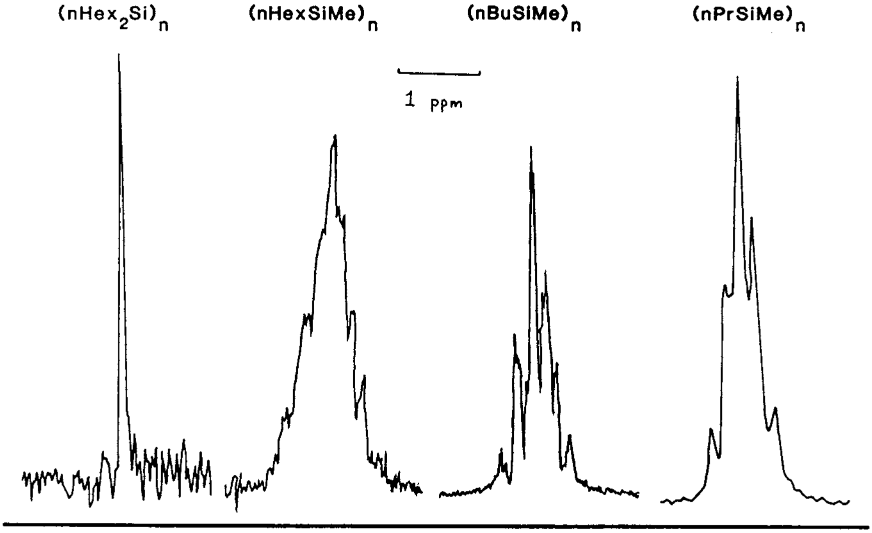
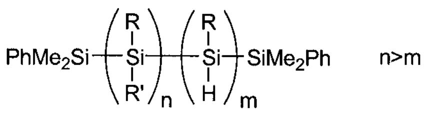


Figure 5.20 ^{29}Si NMR spectra for some alkylpolysilanes. Reprinted by permission from A. Wolff et al., *J. Polym. Sci., Polym. Chem. Ed.*, 1988, *26*, 701. Copyright 1988 John Wiley and Sons, Inc.



5.13

triads (Figure 5.21).[114] The three lines have been assigned as −39.2 = heterotactic (RM = MR.), −39.9 = syndiotactic (RR) and −41.2 ppm = isotactic.[115] Deconvolution of the spectrum shows that the relative intensities are 48 : 14 : 37, rather different from the amounts for an atactic polymer, 50 : 25 : 25. The result agrees however with a model in which a single probability factor determines the configuration of successive stereogenic centers.[116]

Polysilanes with high stereoregularity have not yet been obtained. Partially stereoregular polysilanes have, however, been synthesized by the ring-opening polymerization of stereoisomeric $(PhSiMe)_4$, as described in Section 5.3.5.[33]

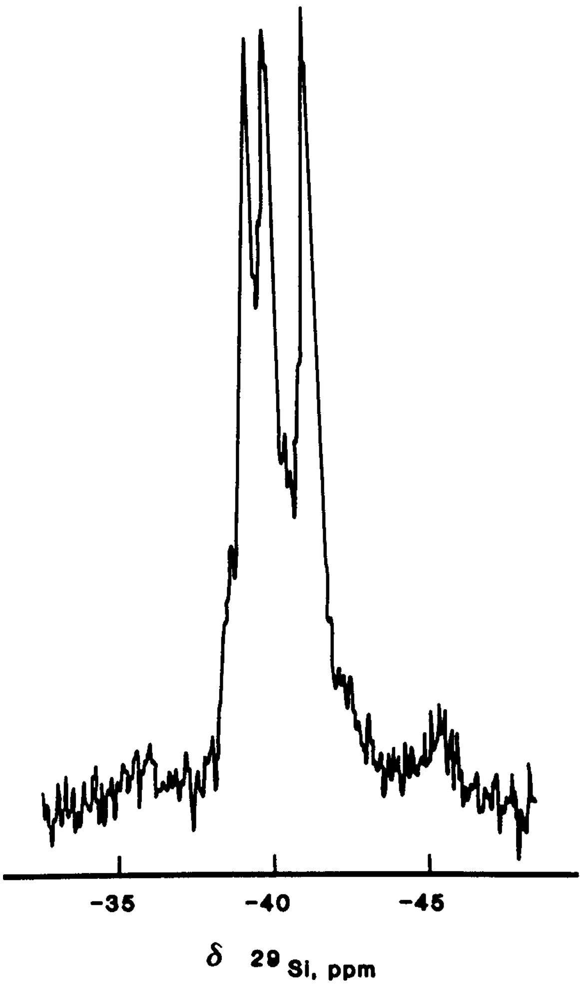
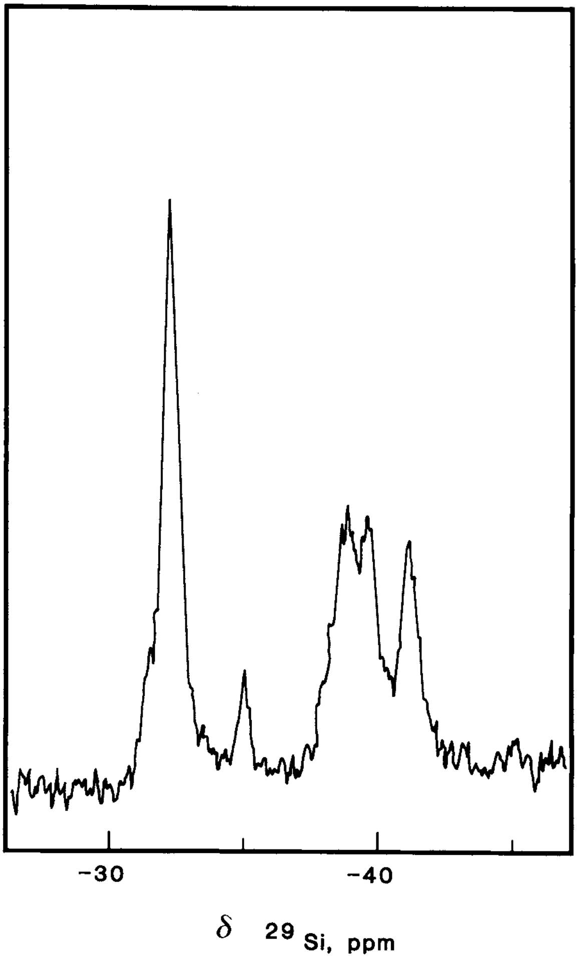


Figure 5.21 ^{29}Si NMR spectrum of $(PhSiMe)_n$. The three principal lines have been associated with the triad arrangements, RM, RR and MM. Reprinted by permission from A. Wolff et al., *J. Polym. Sci., Polym. Chem. Ed.*, 1988, *26*, 713. Copyright 1988 John Wiley and Sons, Inc.

5.12.2 Ordering in Polysilane Copolymers

Copolymers containing more than one kind of silicon atom may have several kinds of arrangements. A copolymer that contains two kinds of silicon atoms might be (1) randomly arranged, or (2) block-like, with long runs of silicon atoms of just one kind, or (3) ordered, with the two kinds of silicon atoms alternating along the chain. Ordering in polysilanes is conveniently studied by ^{29}Si NMR spectroscopy. The usual synthesis by sodium condensation produces either random or block-like copolymers, depending on the relative reactivities of the chlorosilanes. Random copolymers are obtained for similar chlorosilanes, for example *n*-BuSiMeCl$_2$ and *n*-HexSiMeCl$_2$, but if the chlorosilanes have rather different rates of reaction with alkali metal (in the Wurtz synthesis), one will be consumed preferentially to generate block-like copolymers. As an example, the ^{29}Si NMR spectrum for (PhSiMe)$_n$ (*n*-HexSiMe)$_m$ is shown in Figure 5.22. The spectrum shows a peak near that for pure (*n*-HexSiMe)$_m$ as well as the three-line pattern characteristic of (PhSiMe)$_n$, with only weak resonances falling between these two

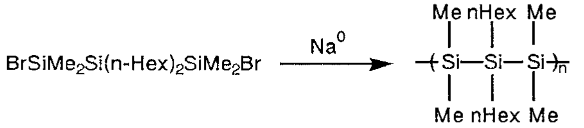
Figure 5.22 ^{29}Si NMR spectrum of (PhSiMe)$_n$-*co*-(*n*-Hex$_2$Si)$_n$, a block-like copolymer.



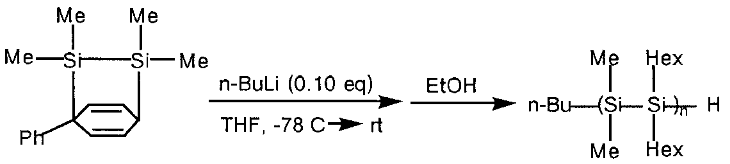
values. The NMR indicates a highly block-like structure, with long runs of similar silicon atoms; this arrangement results because $PhMeSiCl_2$ is very much more reactive than n-$HexSiMeCl_2$.

The ^{29}Si NMR spectrum of polysilastyrene, $(PhSiMe)_n$ $(Me_2Si)_m$, indicates that this polymer also has a rather block-like structure. A much less block-like arrangement in a polymer with the same composition, $(PhSiMe\text{-}SiMe_2)_n$, has been obtained by sodium condensation of the dichlorodisilane $ClSiMe_2\text{-}PhMeSiCl$.[117] Note that $(PhSiMe\text{-}SiMe_2)_n$ is neither a random nor a fully ordered copolymer (it is partially ordered, since no runs of more than two PhSiMe or Me_2Si units occur). The ^{29}Si NMR spectrum, and other physical properties, for this polymer and polysilastyrene are quite different.

A nearly fully ordered polysilane copolymer has been synthesized by careful condensation of a 1,3-dibromotrisilane, yielding the AABAAB-type copolymer shown in equation (30).[118] The best method for obtaining ordered polysilane copolymers is however by the anionic polymerization of masked disilenes (Section 5.3.3). Formation of an ABAB-type copolymer is illustrated in equation (31).[119] These polymers show only two narrow lines in their ^{29}Si NMR spectra, consistent with their ordered structure. In a similar reaction, the Sakurai group synthesized an exactly alternating polysilastyrene polymer, $(PhMeSi\text{-}SiMe_2)_n$.[120]

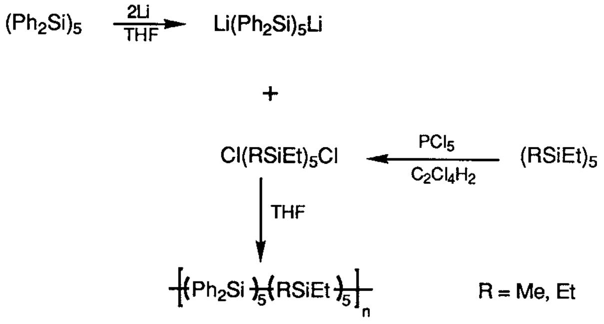


(30)



(31)

Another approach to ordering in polysilanes involves cocondensation of a dilithiopolysilane oligomer with an α,ω-dichloropolysilane, to give a block copolymer, as shown in Scheme 5.6.[121] In principle this method might yield fully ordered polymers, but there is evidence that $Li(Ph_2Si)_5Li$ undergoes redistribution to give $(Ph_2Si)_4$ and shorter Si-Si chains, and the actual degree of ordering of copolymers made by this route has not been investigated.



Scheme 5.6

5.12.3 Network Polysilanes, Polysilane Dendrimers, and Ladder Polysilanes

Most of the research on polysilanes has been concerned with linear polymers with two organic groups on each silicon, $(RR'Si)_n$. However, polymers with only a single organic substituent per silicon, $(RSi)_n$, have been investigated in several laboratories. These "polysilyne" polymers were first prepared at AT&T Bell Laboratories by reduction of alkylchlorosilanes in pentane with an emulsion of sodium-potassium alloy, produced by ultrasound irradiation.[122] Potassium graphite, C_8K, is also a useful reducing agent for polysilyne synthesis.[123] For alkyl groups larger than ethyl, the resulting polymers are soluble in organic solvents such as THF and can be cast into transparent yellow films.

Among the polymers which have been described are the alkylpolysilynes with R = methyl, *n*-propyl, *n*-butyl, isobutyl, *n*-hexyl, cyclohexyl, *a*-phenethyl, as well as the arylsilyne polymers with R = phenyl and *p*-tolyl. Molecular weights are typically 10,000 to 20,000. Water-soluble polysilynes bearing oligoethylene oxide side groups have also been reported.[124] All the polysilynes are visibly colored, yellow or orange, and have electronic spectra differing greatly from those of linear polysilanes (Figure 5.23). Like the linear arylpolysilanes, the arylsilylnes can be modified, for instance by treatment with triflic acid to replace some of the phenyl groups with triflate, and then substituting the triflate groups by nucleophiles.[125] Partially branched polysilanes have also been synthesized, by coreduction of $RSiCl_3$ and R_2SiCl_2.[126]

Polysilynes might adopt an unsaturated structure (RSi=SiR-SiR=Si-SiR), with alternating single and double bonds, analogous to the structure of polyacetylenes. Such polymers would be very interesting, but are disfavored because of the relative weakness of the Si=Si double bonds. All the evidence indicates that the polysilynes have instead a network structure with cross-links as shown in Figure 5.24. In the three-dimensional network each silicon is linked to three other silicon atoms by sigma bonds. The polysilynes

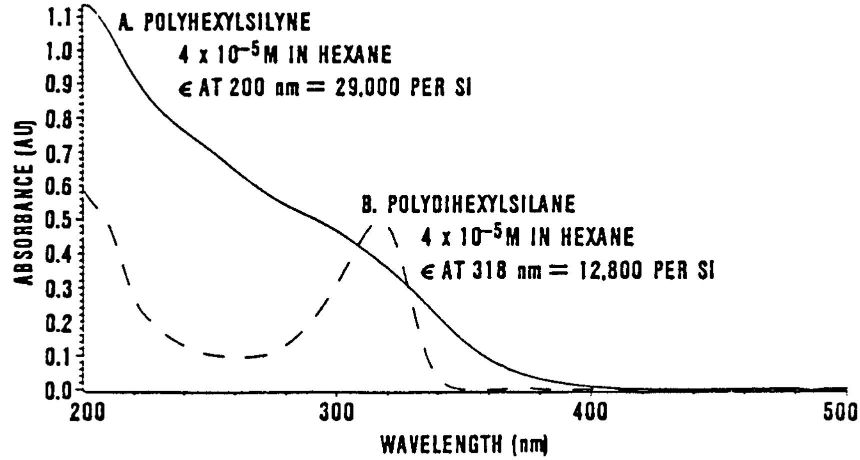


Figure 5.23 Ultraviolet spectra of network polymers $(n\text{-HexSi})_n$ compared with $(n\text{-Hex}_2\text{Si})_n$. Reprinted with permission from Bianconi et al., *Macromolecules* 1989, *22*, 1697. Copyright 1989 American Chemical Society.

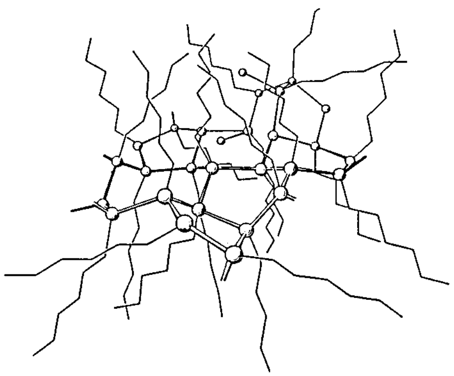
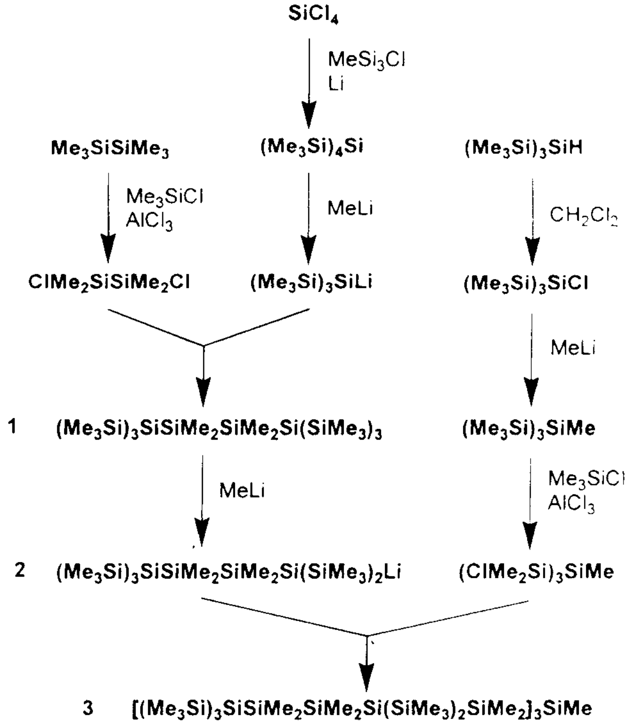
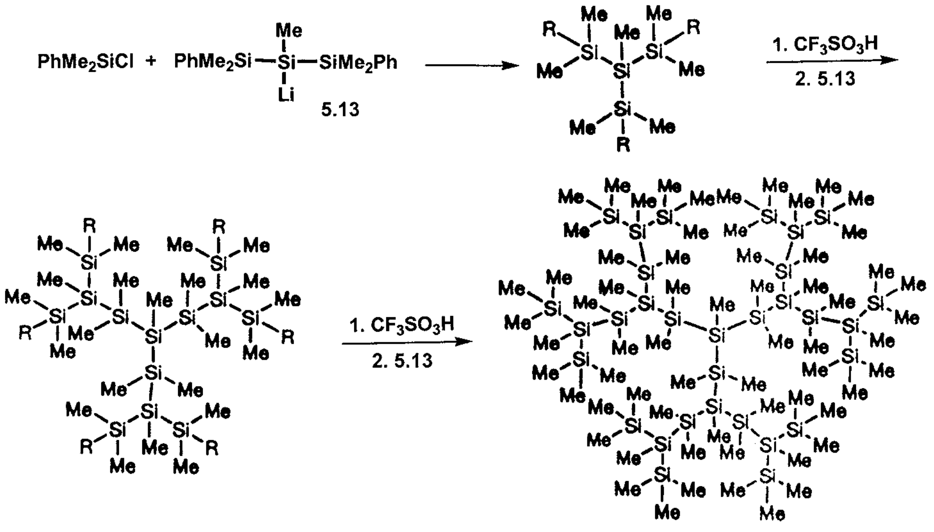


Figure 5.24 The network structure proposed for (n-HexSi)$_n$. Large spheres represent Si atoms. Reprinted with permission from Bianconi et al., *Macromolecules* 1989, *22*, 1697. Copyright 1989 American Chemical Society.

are therefore intermediate between the linear polysilanes, where each silicon is bonded to two others, and elemental silicon in which each silicon forms four sigma bonds to other Si atoms. It follows that the polysilynes should exhibit enhanced electron delocalization, as evidenced in their absorption spectra. Like the linear polysilanes, polysilynes are photoluminescent. A careful study of the photophysics of these polymers indicated that the photoexcitation results in the generation of localized electron-hole pairs, whose recombination leads to the visible luminescence.[127]

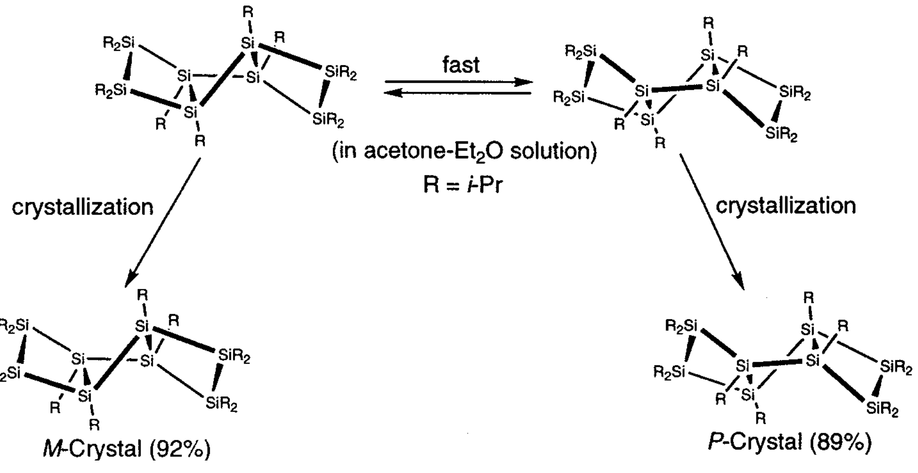


Scheme 5.7 Reprinted with permission from reference 128. Copyright 1995 American Chemical Society.



Scheme 5.8 Reprinted with permission from reference 129. Copyright 1998 American Chemical Society.

In recent years polysilane dendrimers have been synthesized in several laboratories. Two examples are shown in schemes 5.7[128] and 5.8.[129] The dendrimers have electronic absorption spectra similar to those of the longest silicon chains present, but with intensity about ten times as great. Like the network polysilanes, these dendrimers display weak visible emission spectra, perhaps resulting from localized excitations at the branching points. The field of polysilane dendrimers in the subject of a recent authoritative review.[130]



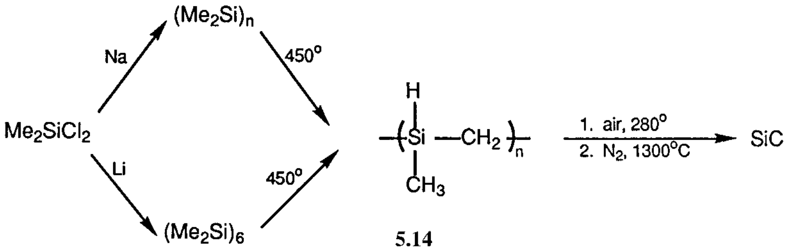
Scheme 5.9 Reprinted with permission from reference 131. Copyright 2000 Elsevier Science.

An interesting series of ladder polysilane oligomers has been developed by Matsumoto and coworkers.[131] These are made by coreduction of dichloro- and tetrachlorodisilanes bearing isopropyl substituents, as shown in Scheme 5.9, and similar Wurtz-type condensation reactions. The ladder oligomers have low oxidation potentials, and for the larger compounds, long-wavelength UV absorption; they form quite stable anion radicals when reduced with alkali metals. A remarkable finding is that the *anti,anti* compound W crystallizes spontaneously into either the M or P enantiomer, and so provide an unusual example of chiral symmetry breaking.

5.13 Technology of Polysilanes

5.13.1 Precursors to Silicon Carbide

The discovery by Yajima that polysilanes could be pyrolyzed to silicon carbide was mentioned in the introduction.[7] In this process, either $(Me_2Si)_n$ or the cyclic oligomer $(Me_2Si)_6$ are synthesized from Me_2SiCl_2 and are then heated to near 450 °C (Scheme 5.10). This discovery has been commercialized by the Nippon Carbon Co. for the production of NICALON™ silicon carbide fibers. In this process, methylene groups become inserted into many of the Si-Si bonds to give a polycarbosilane polymer with the idealized **5.14**.



5.14

Scheme 5.10

The actual structure of the polycarbosilane is more complex, including cross-links through CH groups attached to three silicon atoms. This intermediate polymer is fractionated by precipitation from a solvent to give material with molecular weight 1,800, which can be spun into fibers. These are heated in air to form a skin of SiO_2 on the surface, making the fibers rigid so that they will not melt when pyrolyzed. Further heating to >800 °C converts the polycarbosilane to amorphous silicon carbide; at still higher temperatures, crystallites of β-SiC begin to grow in the ceramic, reinforcing and strengthening the fibers. Maximum tensile strength is attained near 1,300 °C. This technology can also be used for the manufacture of monolithic silicon carbide objects. Modifications of the process include the addition of polyborodiphenylsiloxane as a catalyst and the inclusion of $Ti(O\text{-}i\text{-}Pr)_4$ to give (after pyrolysis) ceramic fibers containing titanium and oxygen as well as silicon and carbon. A more complete description of this technology can be found in a comprehensive review.[132]

Other linear polysilanes can also be used as ceramic precursors. Solid objects of silicon carbide are manufactured by Nippon Soda Co. from polysilastyrene and finely divided silicon carbide powder.[133] These materials are blended, injection molded to the

desired shape using conventional equipment and then pyrolyzed to give silicon carbide with 75–80% of the theoretical maximum density. The 20–25% of void space limits the ultimate strength of the ceramic somewhat, but there is a compensating advantage. The vacant space is present as tiny bubble-like "microvoids," which limit the growth of cracks. As a result, this material is the first silicon carbide which can be further shaped by machining. Polysilastyrene, when photocross-linked, can also be pyrolyzed to form silicon carbide fibers or coatings.

More complex, cross-linked polymers containing silicon-silicon bonds have also been used as silicon carbide precursors. The mixture of methylchlorodisilanes formed in the direct process for synthesis of Me_2SiCl_2 contains the three compounds shown in equation (32). When these are heated with a phosphonium salt catalyst, they undergo a redistribution reaction to give a polycyclic, cross-linked oligomer (**5.15**) having the approximate composition shown, which undergoes pyrolysis to silicon carbide in high yield.[134] In addition a variety of cross-linked polymers have been obtained from alkali metal condensation of mixtures of $CH_2{=}CHSiMeCl_2$ with Me_2SiCl_2, $MeSiHCl_2$, and Me_3SiCl, which produce silicon carbide in good conversion upon pyrolysis.[135]

$$\left.\begin{array}{c} MeCl_2SiSiCl_2Me \\ + \\ MeCl_2SiSiClMe_2 \\ + \\ Me_2ClSiSiMe_2Cl \end{array}\right\} \xrightarrow[250^{\circ}C]{nBu_4P^+Cl^-} \underset{\mathbf{5.15}}{\left[(Me_2Si)_3(MeSi)_{17}Cl_5\right]} \xrightarrow{\Delta} SiC \qquad (32)$$

5.13.2 Polysilanes as Photoresists for Microelectronics

Modern electronic and communications industry depends upon microlithography for the manufacture of microchips and other components. In this process, an image is transferred to a photosensitive layer, called a photoresist, by exposing it through a mask. There are two types of photoresists, as shown in Figure 5.25. Upon irradiation, the photoresist either becomes cross-linked (a negative-working photoresist) or becomes degraded (a positive-working photoresist). Most microlithography at present is done with positive-working photoresists.

As microelectronic components have grown more complex, it has become necessary to repeat this process as many as 25 times to transfer all the necessary information to the microchip. In order to cover existing topography on the chip, it is often preferred to use a bilayer resist system, as shown in Figure 5.26. The silicon wafer, with its existing topography, is first coated with a relatively thick layer of a polymer which is not photosensitive, as a planarizing layer. This is covered with a very thin (0.05 to 0.2 μm) layer of photoresist material. After exposure and development, the image is transferred through the planarizing layer by etching it away with an oxygen plasma. The photoresist layer must not be removed by the oxygen plasma, and this leads to one important advantage of polysilanes as photoresists. During exposure to the plasma, polysilanes (and other silicon-containing polymers) form a coating of silicon dioxide, which

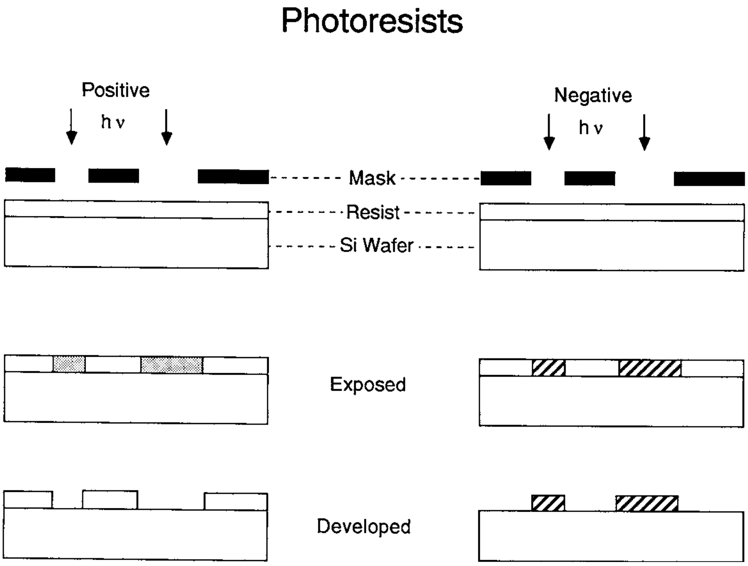


Figure 5.25 Schematic drawing showing the mode of operation of positive and negative photoresists.

protects the underlying polymers from attack by the oxygen ions. The bilayer process makes it possible to generate steep-sided, narrow features desired in modern microchip fabrication.

The polysilanes can be used as photoresists because they undergo scission when exposed to ultraviolet light, as explained in Section 5.10. Both the extinction coefficient and the wavelength of maximum absorption decrease with increasing exposure, so that polysilanes can be "bleached" photochemically, as illustrated for $(n\text{-HexSiMe})_n$ in Figure 5.27. Dialkylsilane polymers are generally better as positive photoresists than

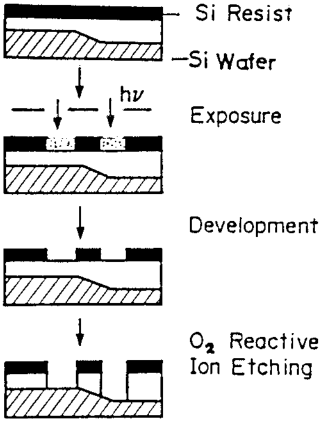


Figure 5.26 Schematic drawing showing the use of a polysilane photoresist in a bilayer construction, above an inert layer which is removed by oxygen ion etching.

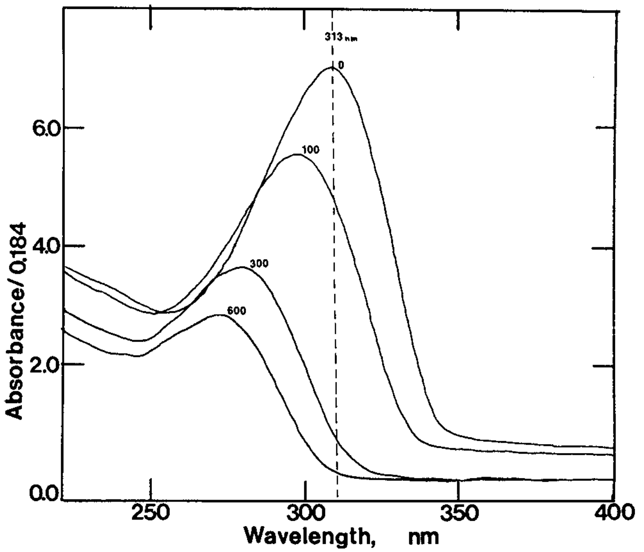


Figure 5.27 Ultraviolet spectra of (*n*-HexSiMe)$_n$ showing bleaching of the absorption band with increasing doses of UV radiation. Reprinted by permission from P. Trefonas et al., *J. Polym. Sci., Polym. Chem. Ed.*, 1983, *22*, 822. Copyright 1983 John Wiley and Sons, Inc.

arylalkyl or diaryl polymers, because the photoscission is not accompanied by cross-linking for the dialkyl materials.[136] An early example of a bilayer composition made using a (cyclo-HexSiMe)$_n$ photoresist generated at IBM-Almaden Research Laboratories is shown in Figure 5.28.[137] Some polysilanes can be developed without the use of a solvent, using UV laser photolysis. Such photoresists are said to be "self-developing."[138]

The disadvantage of polysilanes as positive-acting photoresists is that they do not provide an amplifying effect, so the radiation dose must be relatively large. However, there may be other uses for polysilanes in resist technology. A bottom anti-reflective layer is essential for deep UV lithography, and the polysilane copolymer $(Ph_2Si)_n(PhSiMe)_n$ is very effective in this application.[139] At still higher energies, using cobalt-60 gamma radiation or 20 keV electron beam radiation, the polysilanes (PhSiH)$_n$ and (PhSiH)$_n$(VinylSiH)$_m$ copolymer undergo efficient photocross-linking and so are highly sensitive as negative-acting photoresists, especially when AIBN is added as a free-radical source.[140]

5.13.3 Polysilanes as Photoinitiators

Photolysis of polysilanes produces silyl radicals, which can be used to induce free-radical reactions. Because the silyl radicals can add to carbon-carbon double bonds and begin the formation of polymer chains, polysilanes can be used as radical photoinitiators. In early studies, (PhSiMe)$_n$ and its copolymers $(PhC_2H_4SiMe)_n$ and (cyclo-HexSiMe)$_n$ were shown to photoinitiate the polymerization of styrene and several acrylate

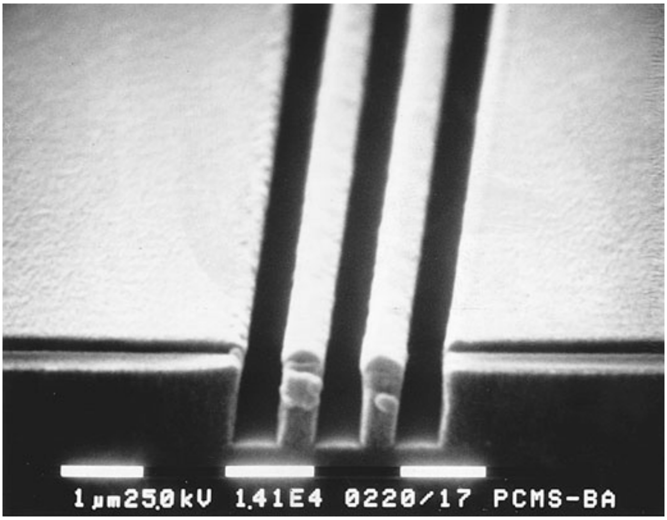


Figure 5.28 Test chip, using a (cyclo-HexSiMe) photoresist in a bilayer construction, after exposure, development and etching. Resolution is about 0.45 µm. Photo courtesy of R. D. Miller.

monomers, using radiation of 254 nm wavelength.[141,142] These studies reported a photoinitiation efficiency of only $\sim 10^{-3}$ (one photon in 10^3 initiating a polymer chain.)

A recent careful investigation shows, however, that the photoinitiation efficiency of polysilanes is much higher than reported earlier. Using 313 (or 346) nm light, $(n\text{-Hexyl}_2\text{Si})_n$ as the initiator and methyl methacrylate as the substrate, Peinado and coworkers obtained initiation efficiencies of 0.18 (0.19), and for styrene at 346 nm, 0.34.[143] This compares with a value of 0.24 for styrene using the conventional photoinitiator, benzoin methyl ether. Thus it now appears that polysilanes are quite efficient photoinitiators for vinyl polymerization. In addition, the polysilanes have higher extinction coefficients than usual photoinitiators, making them effectively more active. Moreover, the polysilanes are less susceptible to inhibition by oxygen than other photoinitiators. As described in Section 5.10, photolysis of polysilanes leads initially to elimination of silylenes (which do not initiate radical chains) and scission to silyl radicals. Many of the radicals are probably lost through recombination; many others under secondary processes that lead ultimately to stable silyl radicals and to Si=C compounds (silenes). Both of these may act to scavenge oxygen during the photoinitiation. Industrial photoprocesses, such as photopolymerization of films and coatings, must ordinarily be carefully protected from oxygen, and this is both difficult and expensive. Because of their relative resistance to the effects of oxygen, the polysilanes may be useful either as photoinitiators or as additives in photoinitiated reactions.

Photopolymerization using polysilanes can also be carried out to yield block copolymers containing runs of silicon atoms, for instance polysilane-methyl methacrylate. The resulting copolymer can then be used as a macro-photoinitiator for further free-radical polymerizations.[144,145]

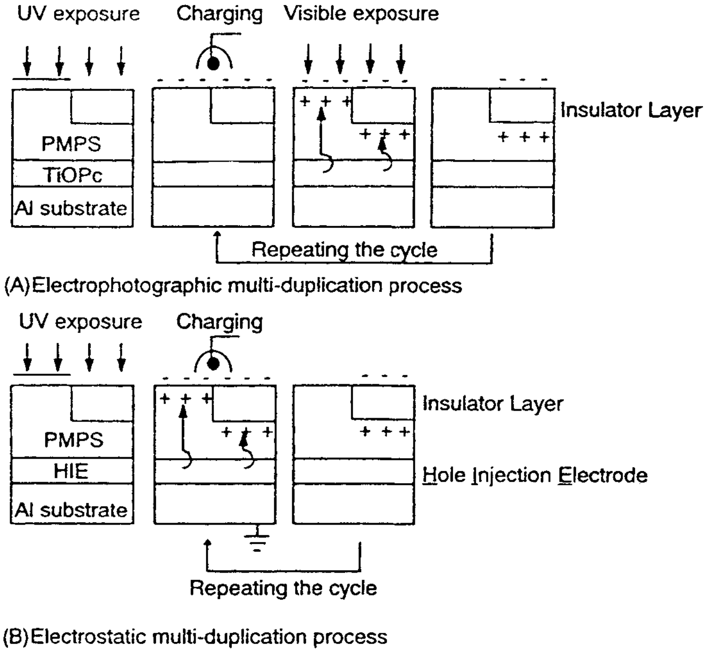


Figure 5.29 Schematic diagram of new multiduplication processes based on polysilanes: (A) an electrophotographic process; (B), an electrostatic process. Reprinted with permission from reference 146. Copyright 2000 Kluwer Academic Pulishers.

5.13.4 Polysilanes in Display Technology

The photoconductivity of polysilanes was described in Section 5.8, and their electroluminescence is covered in Section 5.9.2. These properties make polysilanes possible components of polymer light-emitting diodes, either as charge transport layers or as the actual emissive materials.[146] A drawback of the polysilanes is their photodegradation under ultraviolet irradiation, a problem which must be overcome if polysilanes are to become commercially useful.

The photodegradation of polysilanes can be used to advantage, however, in some applications. Two interesting possibilities are shown in Figure 5.29. A polysilane layer, above a photosensitive charge-generating layer, can be patterned by exposure to UV light through a mask, so that the exposed portion is oxidized to siloxane while the unexposed portion remains as polysilane. Hole transport to the surface is now possible through the unexposed polysilane, but not through the oxidized region. Corona charging followed by exposure to visible light generates a surface pattern of negative charges, which can be transferred to a toner as in usual electrostatic copying. The pattern generated by photo-oxidation is permanent, so repeating the corona charging and visible exposure provides an electrophotographic multiduplication process.[147]

An even simpler duplication process based on the same principle is shown in Figure 5.29(B). If a hole-injecting electrode is used instead of a photosensitive layer, simple electrostatic charging allows the pattern to be read and transferred.[148] Other new technologies based on the photopatterning of polysilanes are being developed, and may become commercialized in the future.

5.14 Additional Readings

Further information about the entire field of polysilanes, cyclic, linear, and high polymeric, can be found in R. West, Chapter 19, "Polysilanes," in *The Chemistry of Organosilicon Compounds*, S. Patai and Z. Rappoport, Ed., Wiley: New York, 1989. An in-depth review of polysilane high polymers emphasizing spectroscopic and other physical characterization and containing extensive tables of data is "Polysilane High Polymers," R. D. Miller and J. Michl, *Chem. Reviews* 1989, *89*, p. 1357. Several useful chapters on various aspects of polysilane chemistry appear in the book, *Silicon-Containing Polymers*, R. G. Jones, W. Ando, and J. Chojnowski, Eds., Kluwer: Dordrecht, Netherlands, 2000. A special issue of *Journal of Organometallic Chemistry* devoted entirely to polysilanes, *A Half-Century of Polysilane Chemistry*, appeared as volume 686 in 2004.

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6

Ferrocene-Based Polymers, and Additional Phosphorus- and Boron-Containing Polymers

6.1 Ferrocene-Based Polymers

6.1.1 Rationale

Ferrocene is an inexpensive, stable molecule with an interesting and reversible electrochemistry. It is synthesized by the metal-hydrogen exchange reaction of cyclopentadiene with sodium followed by treatment of the resultant sodium cyclopentadienide anion with ferrous chloride. The high stability and electroactivity of the ferrocene molecule has prompted numerous attempts to incorporate it into polymer structures. So, too, has the inherent torsional freedom of the cyclopentadienyl groups around the iron atoms and their capacity to serve as swivel group sites. Polymerization attempts range from the addition reactions of vinylferrocene and its derivatives, to condensation reactions, ring-opening polymerizations, and dendrimer assemblies. These will be considered in turn.

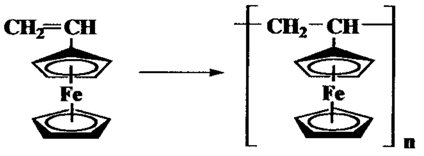
6.1.2 Addition Polymerization of Vinylferrocenes and Other Vinyl Organometallics

General

Considerable effort in the 1970s by Pittman, George, Hayes, Korshak, and others was applied to exploring the addition polymerization of vinylferrocene **6.1** to give organic polymers with pendent ferrocenyl side groups (**6.2** in reaction (1)).[1–6] This type of polymerization reaction has been attempted with the use of free radical, cationic, anionic, and Ziegler–Natta methods.

Free-Radical Initiation

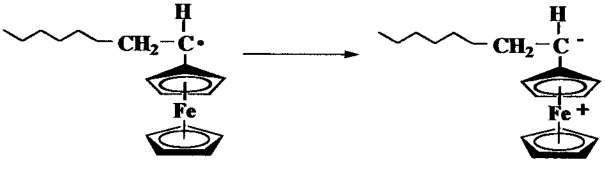
For free radical polymerization reactions, the initiating radicals must be generated from azo-initiators because peroxides cause oxidation of the metal. In polymerizations of the type shown in reaction (2) the side group ferrocene units are the source of both the



6.1 6.2

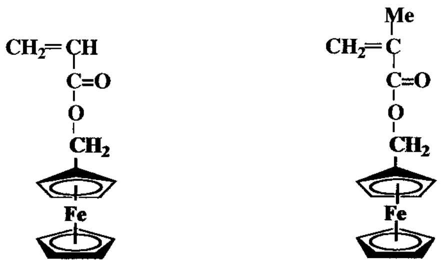
(1)

thermal stability of the product polymers and complications inherent in the free radical polymerization process. For example, electron donation from the iron atoms to a growing radical chain end can convert an active radical (**6.3**) to an anion (**6.4**), which terminates the polymerization. The Fe^{+} center then rearranges to form a paramagnetic, ionically bound Fe(III) species. Ultimately this leads to extensive chain-transfer, limitation of the chain length, and formation of branched structures. This does not occur if the ferrocene unit is insulated from the vinyl group by a spacer unit, as in **6.5** or **6.6**, because these monomers polymerize normally. For example, monomer **6.6** gives polymers with M_n molecular weights as high as 250,000.



6.3 6.4

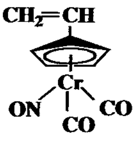
(2)



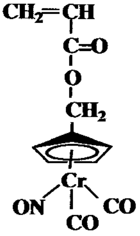
6.5 6.6

However, the electron-transfer process outlined in reaction (2) has serious practical consequences in the free-radical polymerization of **6.1**. First, directly or indirectly, it causes precipitation of the growing polymer chains until, at monomer to polymer conversions of 90% or more, all of the polymeric product is insoluble in most organic solvents. This may not be due entirely to cross-linking because some of the oligomers formed at low conversions are soluble in chloroform.[5] Molecular weights in the range of 6,000–35,000 have been reported for soluble, free-radical-generated poly(vinylferrocenes), which correspond to degrees of polymerization of about 28 to 160. Both vinylferrocene, **6.1**, and ferrocenylmethacrylate, **6.6**, undergo random free-radical copolymerization with styrene or methyl methacrylate to give soluble polymers. With **6.6**, copolymers with M_n molecular weights as high as 250,000 are accessible.

Related organometallic monomers, such as the cyclopentadienylchromium complexes, shown as **6.7** and **6.8**, have also been homo- and copolymerized, using free radical initiation.[7] Here, too, the transition metal in **6.7** generates an electron-rich vinyl group which deactivates the monomer.

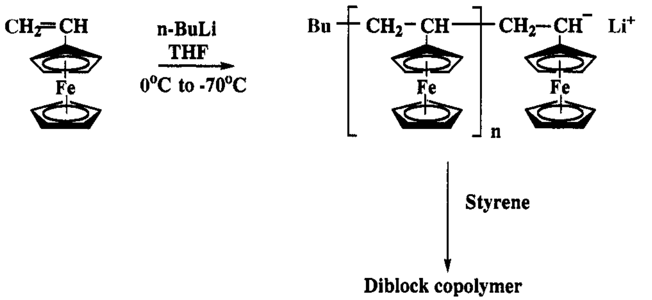


6.7



6.8

More recently Nuyken and coworkers[8] have polymerized highly purified vinylferrocene using anionic initiation. The process is summarized in reactions (3) and (4). Initiation of the polymerization was accomplished with the use of *n*-butyllithium or distyrylsodium or potassium (produced from styrene and sodium or potassium naphthalenide). The reaction takes place in tetrahydrofuran (THF) solvent at −70 °C to 0 °C to give soluble oligomers with molecular weights in the range of 6,000 to 7,500. This corresponds to degrees of polymerization of 28 to 35. The oligo-vinylferrocene produced in this way has a T_g of 219 °C. In addition to the homopolymerization of vinylferrocene, it is possible to initiate the polymerization of vinylferrocene from the active end or ends of anionically produced polystyrene or poly(methyl methacrylate) as shown in reaction sequence (4) to give di- or triblock copolymers. Moreover, the living poly(vinylferrocene) anion initiates the polymerization of styrene to give diblock copolymers.

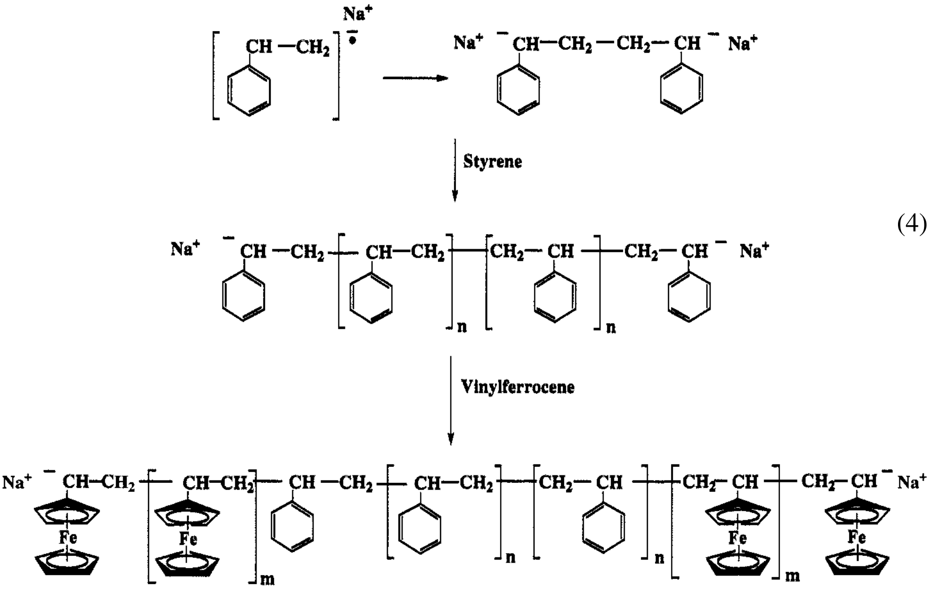


(3)

Note that these organic polymers with metallocenyl side groups are similar in general architecture to the polyphosphazenes with ferrocenyl side groups discussed in Chapter 3 in the sense that the ferrocene units are pendent to the main chain.

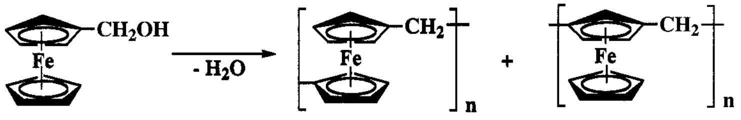
6.1.3 Condensation Polymerizations

Condensation polymerization of functional ferrocenes generally yields medium- or low-molecular-weight polymers with broad molecular-weight distributions.[1,2] For example, ferrocenylcarbinol, **6.9**, has been condensation-polymerized to polymers **6.10** and **6.11** in the presence of boron trifluoride etherate or zinc chloride (reaction (5)).[9,10] Species **6.11**



(4)

appears to predominate in the reaction mixture. The molecular weights were in the range of 2,500 to 6,000, which corresponds to only 13 to 30 repeating units per chain.



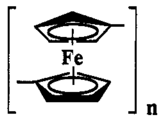
(5)

6.9 6.10 6.11

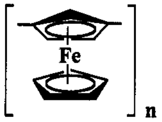
Another condensation approach links cyclopentadienyl rings directly without the presence of a bridging group. Thus, ferrocene, when treated with a peroxide free-radical source is reported to yield species of type **6.12** or **6.13**.[11,12] Perhaps surprisingly, in view of recent work, these polymers showed no significant electronic conductivity. However, oligomer **6.14**, in which a sequence of conjugated units separated the cyclopentadienyl rings, is purple in color.[13] It is possible that the concept of "doping" conductive polymers with oxidizing or reducing agents to generate conductive species was not understood at that time.

Higher molecular weight polymers (40,000–50,000) have been reported from condensation reactions between monomer **6.15** and various silanediols, as illustrated in reaction (6).[2] Polymer **6.16** can be melt-fabricated into films or fibers, which probably reflects the presence of roughly 100 repeating units per chain. However, the separation of the ferrocenyl units by the organic linker groups reduces the influence of the organometallic component.

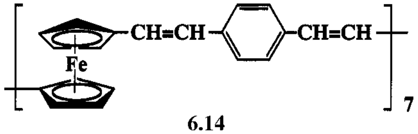
The advantage of these polymers over poly(vinylferrocenes) or related species with pendent organometallic units is that the condensation polymers have ferrocene units in the main chain where they can exert their maximum influence on polymer thermal stability. The disadvantage of the condensation products is that, except in the last example, the molecular weights are too low to favor fiber or flexible film formation. Nevertheless, this work indicated the potential usefulness of polymers with metallocene units in the main chain.



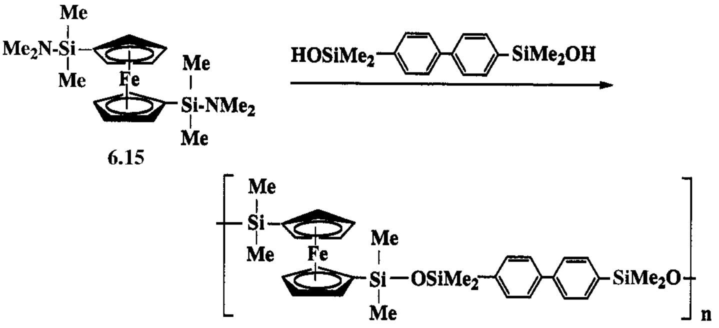
6.12



6.13



6.14



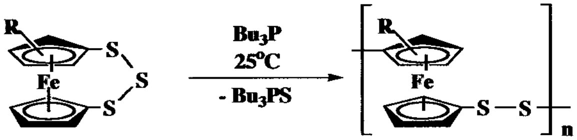
6.15 (6) 6.16

6.1.4 Ring-Opening Polymerization

Synthesis Methods

As discussed, addition and condensation polymerizations generally yield ferrocene-containing polymers that are of relatively low molecular weight. However, research carried out in the 1990s identified a number of ring-opening polymerizations that yield soluble high-molecular-weight polymers—species that can readily be fabricated into films, fibers, and nanostructural materials. In many cases the polymerization reactions are driven by the release of ring strain.

Rauchfuss appears to have been the first to report a ring-opening polymerization that incorporates the ferrocene units into a polymer backbone.[14] Monomer **6.17** reacts at room temperature with tributylphosphine to yield polymer **6.18** via a desulfurization process as shown in reaction (7).

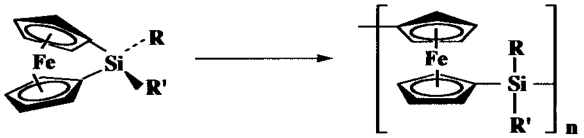


6.17 R = H or *n*-Bu 6.18 (7)

Although polymer **6.18**, where R = H is insoluble, its analogue with R = *n*-Bu is soluble in a variety of organic solvents and has average molecular weights near 40,000 (n = 160) but with a broad molecular weight distribution and with the highest molecular weight values being more than 150,000. This polymer could be reversibly

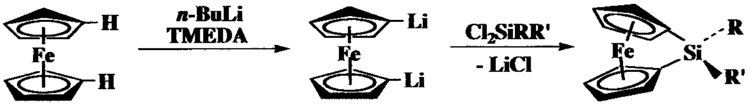
oxidized electrochemically, with the first oxidation occurring at alternating Fe atoms along the chain.

Manners and coworkers have developed the most extensive ring-opening polymerization platform.[15–25] Their method involves the ring-opening polymerization of silicon-bridged ferrocenes ("ferrocenophanes") such as **6.19** to form a wide range of high polymers with the general structure **6.20** as illustrated in reaction (8). These polymers have molecular weights in the 10^5–10^6 range, which corresponds to 500–5,000 repeating units.



6.19 **6.20** (8)

Ring-strain in monomers of type **6.19** can be detected by the marked tilting from coplanarity of the cyclopentadienyl rings.[17,25] This tilting generates approximately 60–80 kJ/mol of ring-strain, which is relieved during polymerization. The monomers are synthesized by the reaction of dilithioferrocene (**6.22**) with a dichlorodiorganosilane, as shown in reaction (9). Dilithioferrocene is produced by deprotonation of ferrocene (**6.21**) with an alkyllithium reagent. Similar techniques are employed to produce monomers with germanium, phosphorus, and sulfur in place of silicon.[17]

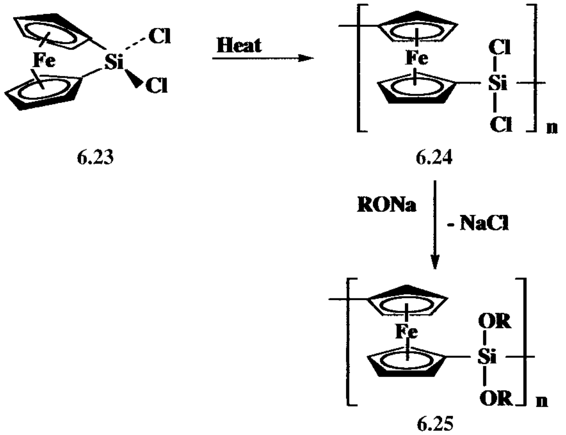


6.21 **6.22** **6.19** (9)

From an experimental viewpoint the polymerization of **6.19**, where R and R′ are both methyl groups, takes place in the bulk (molten) phase in sealed glass tubes at 130 °C and the reactions are complete in less than one hour. The yellow polymer is formed in almost quantitative yield and is soluble in solvents such as THF. The molecular weight is in the range of 3×10^5 to 5×10^5 (1,300–2,000 repeating units).

The polymerizability of **6.19** is relatively insensitive to the types of side groups attached to silicon. For example, side-group combinations that allow polymerization are where R/R′ includes Cl/Cl, H/Me, Me/Me, H/H, Et/Et, Bu/Bu, Hex/Hex, Me/$CH_2CH_2CF_3$, Me/CH=CH_2, Me/$C_{18}H_{37}$, Me/Ph, Me/ferrocenyl, and Me/norbornenyl. Polymerization also occurs with the monomer Ph/Ph at 200–235 °C, but the resultant polymer is insoluble. Moreover, further structural diversity can be achieved via macromolecular substitution reactions that are reminiscent of those used for polyphosphazenes[26] (see Chapter 3). Thus, polymerization of the monomer with Cl/Cl groups on silicon (**6.23**) can be followed by chlorine replacement reactions to give polymeric species with OMe/OMe, OEt/OEt, $O(CH_2)_{11}CH_3$, OPh/OPh, or R_2N/R_2N side units (reaction (10)).

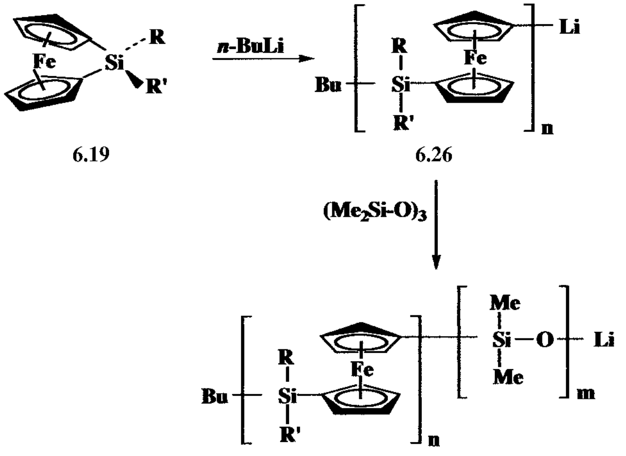
More control over the polymerization process is achieved by anionic rather than purely thermal initiation. Thus, the use of *n*-BuLi as an initiator in THF solvent at 25 °C gives narrow molecular-weight distributions (pdi <1.2), and the molecular weights can be controlled by the ratio of initiator to monomer because each initiator molecule will



6.23 6.24 6.25

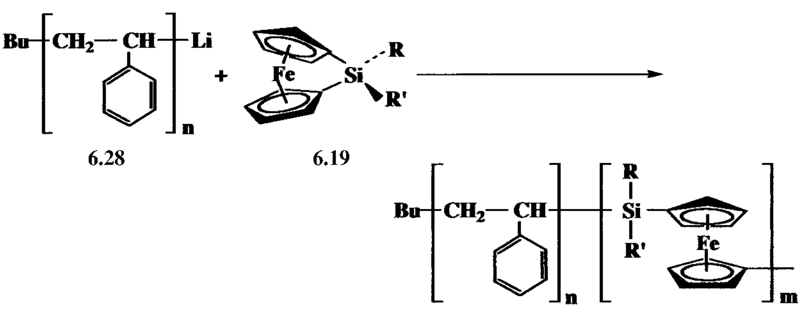
(10)

give rise to only one polymer chain. This polymerization is illustrated in reaction (11), together with use of the living anionic chain end in **6.26** to initiate ring-opening polymerization of a cyclosiloxane to give a block copolymer (**6.27**). Alternatively, the living chain end of anionically produced polystyrene (**6.28**) will initiate polymerization of **6.19** to give styrene-ferrocenylsilane block copolymers (**6.29**) (reaction (12)).



6.19 6.26 6.27

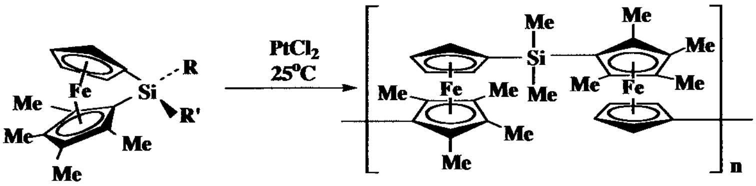
(11)



6.28 6.19 6.29

(12)

In addition to the *n*-BuLi-initiated polymerizations, it is possible to induce ring-opening polymerization using initiators derived from Pt (I), Pt (0), or Rh (I).[17] These are mild initiators that function at room temperature and are believed to participate through the formation of colloidal metal particles. An advantage of these initiators is that they can be used even though the monomer is not exceptionally pure. Molecular-weight control is achieved by the addition of different amounts of Et_3SiH which serves as an end-capper for the chains. These colloidal metal initiators also provide access to regioregular, crystalline poly(ferrocenylsilanes) (**6.31**) from monomers with both cyclopentadienyl and tetramethylcyclopentadienyl (**6.30**) type rings (reaction (13)) (i.e., by CpH-OSi rather than CpMe-OSi cleavage). By contrast, the uncatalyzed thermal process yields regioregular but amorphous polymers.



6.30 6.31 (13)

Properties

The properties of these polymers depend on the two organic side groups linked to silicon and on the element that replaces silicon in the related macromolecules. The glass-transition temperatures of poly(ferrocenylsilanes) are surprisingly low. For polymers with R/R′ on the silicon atoms, the following T_g values have been reported (°C): H/H, 16; Me/Me, 33; Et/Et, 22; Bu/Bu, 3; Hex/Hex, −26; Me/$C_{18}H_{37}$, 1; OEt/OEt, 0; OBu/OBu, −43; OHex/OHex, −51. These low T_g values are attributed to the swivel-group character of the ferrocenyl unit in which virtually free rotation is possible of the cyclopentadienyl rings around the iron atoms. Only when bulky, rigid side groups such as phenyl are present on silicon does the glass-transition temperature rise significantly. For example, the T_g value for the polymer where R/R′ is Me/Ph is 90 °C. Some of the polymers with symmetrical substitution at silicon are crystalline. Thus, where R/R′ is H/H, the T_m = 165 °C, Me/Me = 122–145 °C, and Et/Et = 108 °C. Evidence has been obtained from X-ray crystal structure analysis of both short chain models and high polymers that the chains in the crystalline polymers Me/Me and Bu/Bu pack in a trans-planar zig-zag conformation.[27,28]

The electrochemical behavior of poly(ferrocenylsilanes) has been studied at three levels—in solution by cyclic voltammetry, as films deposited on electrodes, and in the solid state via iodine doping. Solution cyclic voltammetric oxidation and reduction has shown that the polymer, where R/R′ is Me/Me, reversibly oxidizes in methylene chloride in two stages, apparently with the first oxidation being on alternating iron atoms along the chain.[29] Films cast on electrodes behave in a similar way and also show an electrochromic response to oxidation and reduction.[30]

Moreover, it has been shown that iodine doping of poly(ferrocenylsilanes) and their germanium analogues converts them from electrical insulators (conductivity ~ 10^{-14} S/cm) to semiconductors (10^{-3} to 10^{-5} S/cm).[31] The color changes from pale yellow to dark brown as iodine doping progresses and as the conductivity rises. Mossbauer spectroscopy suggests that the doping process involves the oxidation of alternating iron centers along each chain.

Applications

A number of different uses have been proposed for these polymers. First, it has been demonstrated that electronic communication exists between the iron atoms along the polymer chains, even though that communication is mediated by the intervening silicon atoms. Thus, as mentioned above, partial oxidation of the solid polymer leads to a large increase in electronic conductivity to 10^{-3} or 10^{-4} S/cm due to hole transport. Applications for these polymers as charge-dissipation coatings have been suggested.[20]

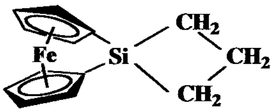
Poly(ferrocenylsilanes) with methoxyethoxyethoxy or quaternary ammonium groups on silicon are hydrophilic or soluble in water and display lower critical solution temperature (LSCT) behavior—again, a similarity to polyphosphazenes[26,32,33] (see Chapter 3).

Attempts have been made to deposit water-soluble poly(ferrocenylsilanes) on surfaces via layer-by-layer self assembly.[17] Block copolymers of poly(ferrocenylsilanes) with poly(ethylene oxide) self-assemble in aqueous media to form redox active micelles.[17]

Cross-linked electroactive gels have been produced by the addition of a spirocyclic ferrocenophane, **6.32**, into the polymerization of **6.19** (R/R′ = Me/Me).[25] These cross-linked polymers absorb organic liquids to form organogels, with the Fe.....Fe distances varying with the degree of swelling. Thus, the reduced form of the polymer gel is a deep red-orange color from a d-d transition at 440 nm. Electrochemical oxidation generates a deep blue color. It is suggested that the degree of swelling of the gels may change with oxidation or reduction and hence open the possibility of formation of electrochemical actuators.[17,25]

Cross-linked microspheres of poly(ferrocenylsilanes) have been prepared by the copolymerization of monomer **6.19** (R/R′ = Me/Me) with spirocyclic cross-linker species **6.32** in a xylene-decane solvent system in the presence of a Pt(0) catalyst.[23] At 60 °C during an 18-hour period, the cross-linked polymer precipitated as 2 μm diameter microspheres. These undergo color changes from orange to green when oxidized by iodine to positively charged species. The oxidized poly(ferrocenylsilane) microspheres self-assemble with negatively charged 0.4 μm silica microspheres to give systems with the larger organometallic spheres forming the core around which the silica spheres are assembled. Manners, Ozin, and coworkers[21] also demonstrated that microspheres obtained by copolymerization of **6.19** and **6.23** can be pyrolyzed at 600 °C to give superparamagnetic iron clusters. However, when formed at 900 °C, the clusters were larger and showed ferromagnetic behavior at room temperature. Such clusters might be used in magnetic recording media. Pyrolysis of similar polymers within the confined channels of hexagonal mesopore silica yielded smaller particles of superparamagnetic α-Fe with thermally induced reorientation detectable at room temperature.

Manners, Winnick, and their collaborators[22] have studied the self-assembly into cylindrical micelles of block copolymers formed from poly(ferrocenylsilanes) (R/R′ = Me/Me) and poly(dimethylsiloxane). By ensuring that the poly(dimethylsiloxane)



6.32

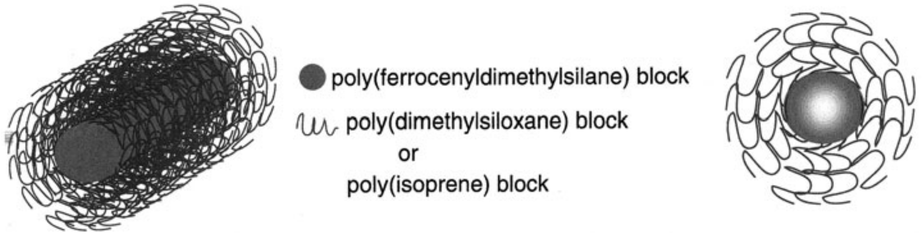


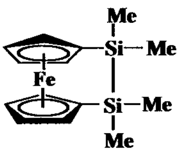
Figure 6.1 Cylindrical micelles of a poly(ferrocenyldimethylsilane)/poly(dimethylsiloxane) or polyisoprene block copolymer showing the central core of the ferrocenylsilane units and the corona of the organic polymer blocks. Reproduced by permission of Prof. I. Manners.

blocks are longer than the poly(ferrocenylsilane) blocks, it was possible to generate cylindrical micelles in warm hexane. These exist in the form of "worm-like" structure with the potentially semiconducting poly(ferrocenylsilane) blocks embedded within an insulating core of the silicone (Figure 6.1). These are being considered for semiconductor applications in which worms are deposited along grooves in a resist layer on a silicon substrate. Hydrogen plasma etching then leaves linear ceramic structures on the surface of the silicon. This was considered to be a first step in the production of nanowires.

Pannell and coworkers[34] described the use of poly(ferrocenylsilanes) as coatings in optical fiber gas sensors. In these devices a small change in refractive index of the polymer film results in a large change in the optical transmission of a tapered optical fiber. This is useful for remote sensing of ammonia or carbon dioxide. Polymers of type **6.20** with R/R′ = Me/Ph and copolymers from monomers with R/R′ = Me/Ph and Me/Me were found to be effective for this application.

Attempts have been made to polymerize other monomers related to ferrocenophanes. Diaz, Pannell, and coworkers[35] found that the presence of two silicon atoms in the ring (**6.33**) inhibited polymerization. However, the analogous carbon ferrocenophane (**6.34**) was shown by Nelson, Rengel, and Manners to polymerize at 300 °C.

Grubbs, Lewis and coworkers[37] attempted to produce highly conjugated polymers via the ring-opening metathesis polymerization (ROMP) of monomer **6.35** to polymer **6.36** (reaction (14)). Although ring-opening oligomerization occurred, the insolubility of species with more than ten repeating units limited the scope of this reaction. Nevertheless, iodine-doped films of these oligomers showed conductivities in the range of 10^{-4} S/cm. It was speculated that this (relatively low) conductivity reflects interchain hopping of holes rather than charge migration along the chains. Thus, the generation of conjugated polymers with higher conductivities probably requires the synthesis



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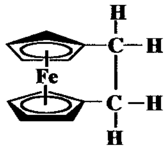

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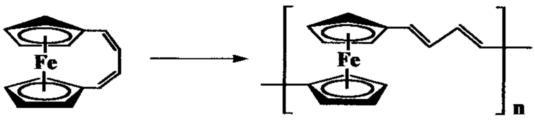
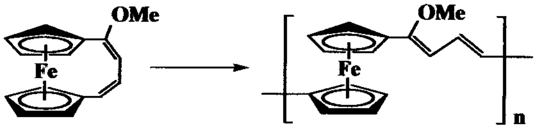
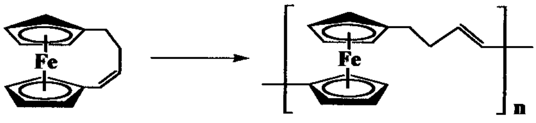


6.35 6.36 (14)

of macromolecules with much higher degrees of polymerization. Polymer solubility can be increased by the linkage of a methoxy group to the monomer (**6.37**), as shown in reaction (15). Polymer **6.38** is soluble in organic media and this offers the prospect that longer chain species can be generated by ROMP techniques.



6.37 6.38 (15)

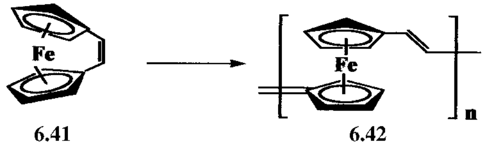


6.39 6.40 (16)

Polymerization of **6.39** to **6.40** (reaction (16)) was less facile, probably because of reduced ring strain in **6.39**. Again, oligomers with chain lengths of only ten repeating units were obtained, which showed conductivities of only 10^{-5} S/cm when doped.

Buretea and Tilley carried this approach one step further with the ROMP polymerization of strained monomer **6.41** (reaction (17)).[38] Polymer **6.42** is insoluble in a wide range of organic solvents. Addition of iodine changed the color of the solid from orange to metallic gray and generated a conductivity of 10^{-3} S/cm. Monomer **6.41** could also be block copolymerized with norbornene to yield moderately soluble polymers. Electrochemical experiments suggested electronic interactions along a chain of atoms in the ferrocenyl-containing block, but doping with iodine resulted in only weak conductivity.

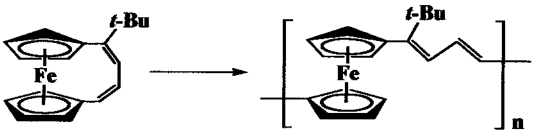
Further investigations along the same lines were reported by Lee and coworkers[39] who polymerized monomer **6.43** using a ROMP catalyst to yield polymer **6.44**, a deep red material that is soluble in benzene or THF (reaction (18)). Presumably the *t*-Bu side groups help to maintain solubility. The M_w values were in excess of 300,000 (~1,000 repeating units), and flexible films of the polymer could be solution cast (a sign of high-molecular-weight chains).



6.41 6.42 (17)

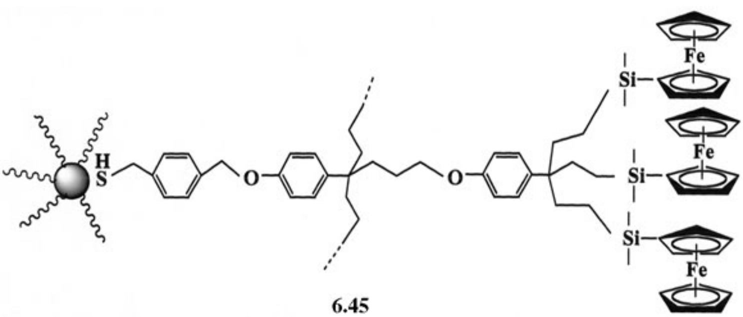
6.1.5 Ferrocenyl Dendrimers

Finally, ferrocenyl units have been incorporated into the perimeter of dendrimeric polymers by Astruc and coworkers.[40] Gold nanoparticles form the core of the dendrimers, with the branched units with terminal ferrocene units coordinated to the gold surface via



6.43 6.44 (18)

thiol linkages. The basic building block is shown in structure **6.45**, and the overall architecture is illustrated in Figure 6.2. Two different forms of the dendrimer are reported—one with 180 and the other with 360 ferrocene units at the periphery. Cyclic voltammetry of dendrimer-modified electrodes was employed for the detection and titration of $H_2PO_4^-$ and adenosine-5′-triphosphate.



6.45

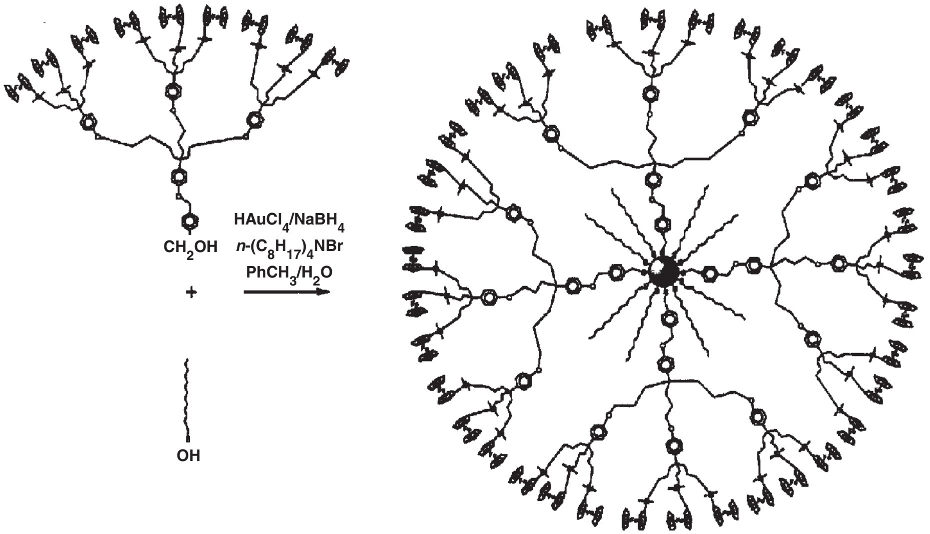


Figure 6.2 Dendrimer and component segments with branched arms radiating from a gold nanoparticle, and with ferrocene units at the perimeter of the nanosphere. From Astruc et al., reference 40. Reproduced with permission.

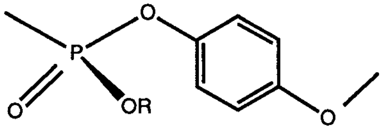
6.2 Other Phosphorus-Containing Polymers

Elemental phosphorus itself exists in several polymeric forms. If the white allotropic form, which consists of P_4 tetrahedral molecules, is put under high pressure, preferably at elevated temperatures, it can be catalytically converted to other modifications.[41] It first becomes red, then violet, then black as the degree of polymerization increases. These materials are very difficult to characterize because of branching and the formation of cyclics. In the extreme limit, the structure approaches that of graphite, and shows good electrical conductivity.[42] No evidence exists at all for the formation of high-molecular-weight, linear chains of elemental phosphorus.

Like other elements important in inorganic chemistry, phosphorus is used mainly in combination with other elements in a polymeric chain.[43,44] Small amounts of phosphorus in a polymer can be greatly advantageous, imparting flame retardancy, improved adhesion to metals, and ion-binding characteristics. Phosphorus-containing polymers are therefore extensively used as flame retardants for fabrics, as adhesives, and as ion-exchange resins.

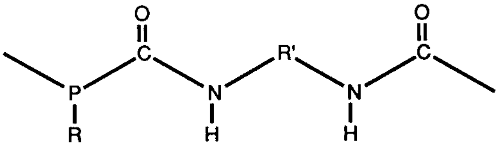
One of the most direct ways for the introduction of phosphorus into a polymer is by direct phosphorylation, for example by reaction of the polymer with phosphorus trichloride and oxygen. This has been done with many classic thermoplastics such as polyolefins and acrylics, common thermosetting materials such as the polyester resins and epoxies, polysaccharides such as cellulose derivatives, and biopolymers such as proteins.[43] However, these materials are better considered to be modified organic polymers, rather than as inorganic or semi-inorganic polymers.[45] Phosphorus is thought to form chains with side-group organic units (with repeat unit -PR_2-), analogous to the polysilanes, but the molecular weights are very low.[46] There have also been some reports describing phosphorus-nitrogen backbone polymers having the saturated repeat unit -RPONR′- (as distinct from that of the phosphazenes covered in Chapter 3), but such materials have been studied in detail.[44]

Some phosphorus-sulfur compounds have been prepared, but thus far these are oligomeric cage-like structures rather than linear or branched chains. Examples are P_4S_3, P_4S_5, P_4S_7, and P_4S_{10}.[42] Aromatic polyphosphates can be prepared from phosphodichloridates ($ROPOCl_2$) and aromatic diols. A typical aromatic polyphosphate, or "phoryl resin," is shown in **6.46**.[42] Although they have some attractive properties, such as good transparency and hardness, they lack long-term hydrolytic stability.



6.46

This problem has been partially overcome by elimination of the phosphorus-oxygen bonds, as, for example, in the poly(phosphinoisocyanates), which have the structure shown in **6.47**.[42] It is also possible to form poly(metal phosphinates) with repeat unit -$M(OPR_2O)_2$- by allowing a metal alkoxide to react with a phosphinic acid.[43] Typical metal atoms are aluminum, cobalt, chromium, nickel, titanium, and zinc.[43] Polymeric phosphine oxides can be prepared by the reactions



6.47

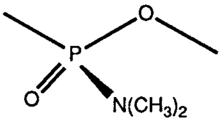
$$xRPCl_2 + nxCH_2{=}CR'R'' \rightarrow [\text{-}PRCl_2(CH_2CR'R'')_n\text{-}]_x$$
$$[(\text{-}CH_2CR'R'')_n\text{-}]_x + xH_2O \rightarrow [\text{-}PR(O)(CH_2CR'R'')_n\text{-}]_x + 2xHCl \quad (19)$$

The materials obtained are extremely stable,[43] because the electron pair of the phosphine structure has been donated to an oxygen atom. A final series of chains of this type are the poly(phosphorylamides). An example, the poly(phosphoryldimethylamide) chain, is shown in **6.48**. These polymers have interesting elastomeric properties, but presumably are hydrolytically sensitive.[42]

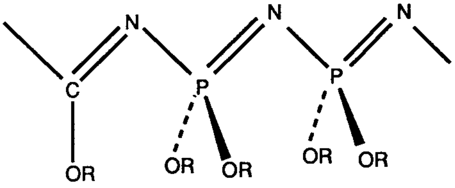
As discussed in Chapter 3, some other inorganic polymers also contain phosphorus atoms.[47] They are derived from the basic phosphazene structure described in Chapter 3, and are obtained by the ring-opening polymerization of heterocyclic compounds in which one of the disubstituted phosphorus atoms is replaced by another moiety. Specifically, introduction of a carbon atom can yield poly(carbophosphazenes), with the repeat unit shown in **6.49**. Alternatively, replacement with a sulfur atom can yield a poly(thiophosphazene) (**6.50**). Relatively little is known about these polymers at the present time.[47]

The newest series of polymers based on a phosphorus-carbon backbone are poly(methylenephosphines) of structure $[\text{-}P(R)\text{-}CR'_2\text{-}]_n$, produced by the polymerization of phosphaalkenes, $P(R){=}CR'_2$.[47a] These polymers react with oxygen to form species of type $[\text{-}P(R)(O)\text{-}CR'_2\text{-}]_n$. A related polymer with phenyl rings in the backbone has also been described.[47b] This is a pi-conjugated polymer with P=C bonds in the main chain.

Another series of polymers that contain phosphorus are the polyphosphates, which have structures very similar to silicates. Some of these are well known as "Graham's salt," "Kurrol sodium salt," and "Maddrell salt."[41] Their linear chains are illustrated in **6.51**. They have not been studied extensively, possibly because they readily undergo molecular reorganization and hydrolytic cleavage to low-molecular-weight materials. In fact, most of the high-molecular-weight species are mixtures of linear oligomeric chains, cyclics, and cross-linked network segments. Also present are strongly bonded countercations. Some of these materials exhibit chelating properties, and are therefore used in metal fabrication and protection.[43] However, the polyphosphates are unusually interesting chain molecules, in that they are totally inorganic, are polyelectrolytes, and contain repeat units of great importance in biopolymeric materials such as the polynucleotides. The skeletal P-O bonds have a length of 1.62 Å, with bond angles of 130° at the O atoms and 102° at the P atoms.[48,49] This inequality in skeletal bond angles is a frequent occurrence in inorganic polymers, as already mentioned with regard to the polysiloxanes, and can have a profound effect on the configurational characteristics of the chains. Specifically, this structural feature causes the all-*trans* conformation of the molecule (often the form of lowest conformational energy) to approximate a closed polygon. Since the difference in bond angles in this case is 28°, it takes approximately 13 repeat units to complete the 360° required for the chain to close on itself.



6.48



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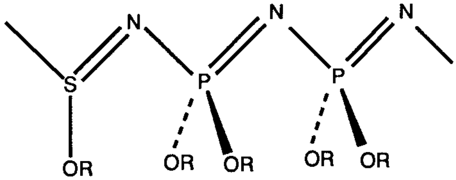
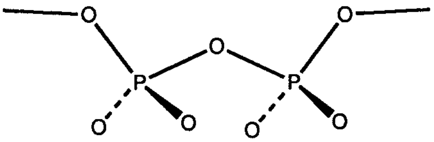


6.50



6.51

The potential barrier that hinders rotations about the skeletal bonds in polyphosphates is relatively small, probably less than 1 kcal mol^{-1}. Nonetheless, the rotational isomeric state model has been used for this chain, since it represents a reasonable approximation to the continuous range of rotational angles.[50,51] Conformational energy calculations, including both steric and coulombic interactions, indicate that *gauche* states were of essentially the same energy as *trans* states when neighboring states remained *trans*. However, consecutive *gauche* states of either like or opposite sign are almost entirely suppressed, by steric interferences, coulombic repulsions, or both.[48–51]

Although this chain model is rather simple, it gave a good account of the relatively large values of the characteristic ratio (7.1 and 6.6) reported for lithium polyphosphate and sodium polyphosphate ("Graham's salt"), respectively. In brief, there are numerous *gauche* states present along the chain backbone, because of their relatively low energy. They generally do not occur in pairs (which are compact) because of the relatively high energies of such conformations. They represent departures from the all-*trans* form of the chain, which has a very small end-to-end distance. It is their presence that explains the relatively high spatial extension of the polyphosphate chain.

Theoretical and experimental studies have also been carried out on sodium phosphate.[48] Theoretical values for molar cyclization constants for the oligomeric molecules were calculated using the rotational isomeric state model. Specifically, calculations

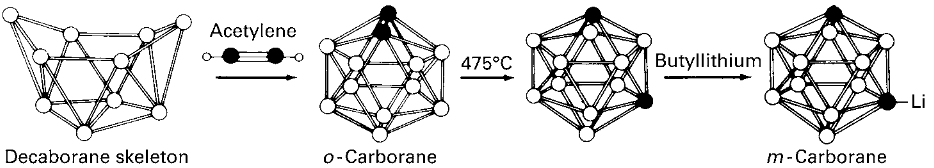
were made of the probability that a polyphosphate chain of the specified length would cyclize. More specifically, the calculations gave the total number of conformations with terminal atoms in sufficiently close proximity to form the final bond completing the cyclic molecule. The calculations were carried out using direct enumeration techniques and, alternatively, using a Gaussian distribution for the end-to-end distances. The calculated results were in satisfactory agreement with experiment.[48,49]

6.3 Boron-Containing Polymers

A variety of polymers contain the element boron.[42,44,52-60] One of the simplest consists of chains of boron fluoride, of repeat unit -BF-, and can be prepared by the reaction of elemental boron with boron trifluoride at high temperatures. The polymer is a rubbery elastomer, but it has been little studied because of its hydrolytic instability and tendency to ignite spontaneously in air.[42] However, a variety of other structures are formed with a number of metals, for example chains with Fe, ladders with Ta, sheets with Ti, tetragonal structures with U, and cubic structures with Ca and Ar. Boron also forms chains that are analogues of poly(dimethylsiloxane), with repeat unit -BCH-O-.[42]

One important class of boron-containing polymers are those which contain the carborane cage, of structure -$CB_{10}H_{10}C$-. This group is prepared by the addition of acetylene to pentaborane or decaborane, -$B_{10}H_{14}$-. The resultant *o*-carborane rearranges to *m*-carborane, as shown in reaction (20).[61] Reactive sites can be introduced by conversion of this product to *m*-$LiCB_{10}H_{10}CLi$, by reaction with butyl lithium. For example, it has been incorporated between siloxane chain units by reaction with a dichlorosiloxane. This gives increased stability to the resulting copolymeric elastomer. Although the transition temperature of this copolymer, like any other, depends on composition,[62,63] the copolymers produced in this way can have a melting point of around 460 °C. Such materials have useful properties, at least for limited periods of time, at temperatures as high as 500 °C. They also have relatively low glass-transition temperatures, around −30 °C, as required in many high-performance applications.[64]

The decaborne cage structure has also been used with some comonomers, specifically diamines, to give relatively high molecular weight polymers. Fibers formed from these chains can be pyrolyzed to give products that consist largely of boron nitride, BN.

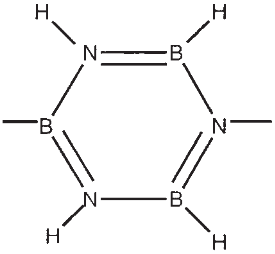


(20)

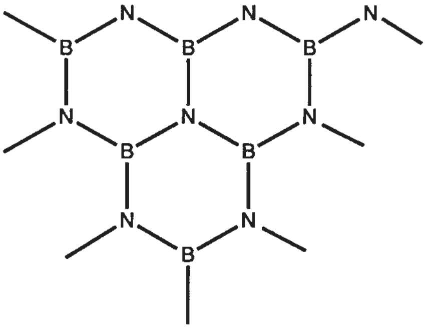
The pentaborane cage structure -B_5H_9- has been used as a side group in the preparation of vinyl-type polymers, but only of relatively low molecular weight. Pyrolysis of this material gives primarily boron carbide, B_4C.

Another example is the poly(borazine) chain, with repeat unit -BRNR-.[53,65] The synthesis of tractable, unbranched polymers of this type is complicated by the formation of borazines, which are very stable cyclic molecules, [$(RBRN)_3$]. This problem can

possibly be overcome through the use of cyclic mono- and diborylamines.[65] Some of these polymers are thermally stable, up to approximately 500 °C, but are easily hydrolyzed. Their most important use is probably as precursors to boron nitride ceramics (see Chapter 9).[53] A related polymer is polyborazylene, which is a cyclo-linear boron-nitrogen analogue of polyphenylene. The simplest structure proposed, which corresponds to $[\text{-}B_3N_3H_4\text{-}]_x$, is shown in **6.52**. Two final examples are boron nitride itself, -BN-,[52,66] and boron phosphide. Boron nitride can be prepared by heating borax ($Na_2B_4O_7$) in the presence of ammonium chloride at 1000 °C.[42] It is thought to have a planar structure similar to that of graphite, as is illustrated in **6.53**. It can be converted into a cubic, diamond-like structure called borazon. It is resistant to hydrolysis and oxygen, and can be harder than diamond.[41] Also, it can be used at temperatures as high as 2000 °C. It is used mainly as a refractory material, abrasive, or insulator.



6.52



6.53

It is also possible to prepare all-carbon polymers of closely related structure. For example, pyrolysis of polyacrylonitrile, $(\text{-}CH_2CHCN\text{-})_x$, first results in cyclization of some of the -CN side chains.[61] Prolonged pyrolysis yields very pure graphitic material. It is very strong and has high thermal stability. In the form of fibers, it can be used for reinforcement in high-performance composites. Additional information on pyrolysis is given in Chapter 9.

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7

Miscellaneous Inorganic Polymers

7.1 Introduction

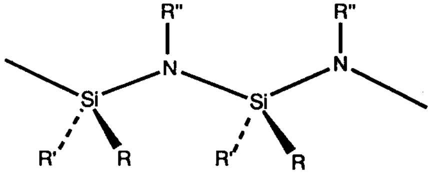
The polymers discussed in this chapter are simply those that do not fit into one of the earlier, more general categories.[1–31] They are generally polymers that are not yet of great commercial importance, often because they are so new that much more research needs to be done before they can be utilized effectively.

7.2 Other Silicon-Containing Polymers

It should be mentioned first that a number of minerals, and glass itself, contain silicon and consist of polymeric structures.[11] Glass is a highly irregular material that consists of rings and linear chains of silicate units in complicated three-dimensional arrangements. On the other hand, some minerals consist of single chains or double chains in which negatively charged oxygen atoms are neutralized by positively charged metal cations. It is sometimes possible to make such materials more tractable by breaking open the cross-links and inserting non-ionic, non-polar groups in their place.[14] Nonetheless, these materials generally are not synthesizable, characterizable, and processable in the way that most organic or inorganic-organic polymers are.

The most important class of silicon-containing polymers that have not yet been covered are the polysilazanes, shown in **7.1**. These polymers, or precursors to them, are generally prepared by the reaction of organic-substituted chlorosilanes with ammonia or amines as is shown in reaction (1).[32]

$$R_3SiCl + 2R'_2NH \rightarrow R_3SiNR'_2 + R'_2NH_2 + Cl^- \qquad (1)$$



7.1

Such molecules can also be formed by the dehydrocoupling reaction catalyzed by bases or transition metals (reaction (2)):

$$R_3SiH + R'_2NH \rightarrow R_3SiNR'_2 + H_2 \tag{2}$$

Another possibility is to use a deamination/condensation reaction, as shown in reaction (3).

$$2R_2Si(NHR')_2 \rightarrow (R'NH)R_2SiN(R')SiR_2(NHR') + R'NH_2 \tag{3}$$

As a final alternative, a redistribution reaction, as illustrated in reaction (4), can be employed.

$$2RSiCl_2 + (R_2SiNH)_3 \rightarrow ClR_2SiNHSiR_2Cl + Cl(R_2SiNH)_2SiR_2Cl \tag{4}$$

The application of these approaches to the formation of the corresponding polymers is illustrated by reaction (5)[32]

$$CH_3NH_2 + H_2SiCl_2 \rightarrow [\text{-}H_2SiNCH_3\text{-}]_x + 2HCl \tag{5}$$

with molecular weights in the vicinity of 10^3 g mol^{-1}. Such oligosilazanes can be used in a dehydrocoupling reaction catalyzed by a transition metal to obtain higher degrees of polymerization.

It is also possible to form novel polysilazanes by dehydrocyclodimerization of the ammonolysis product of CH_3SiHCl_2, or coammonolysis products of this silane with other chlorosilanes.[33] Ring compounds that contain the desired Si and N atoms may also be used as starting materials, followed by hydrolysis, thermolysis, polymerization, or copolymerization to convert them into silazane-type materials. Examples are cyclic *bis* (silyl) imidates, *N*-acylcyclosilazoxanes, *N*-arylcyclosilazoxanes, and *N,N'*-diarylcyclosilazanes.[34]

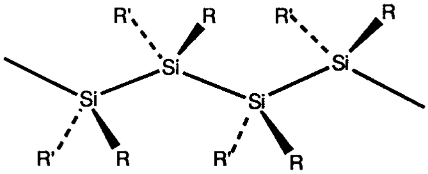
More complicated materials can be derived from the polysilazane structure. Some, like poly(methyldisilylazane), are highly cross-linked, polycyclic structures that are presumably also cage-like. These polymers are soluble in some solvents. Hence, gel permeation chromatography (GPC) measurements have given some information on their molecular weights and molecular weight distributions. ^{29}Si and ^{13}C nuclear magnetic resonance (NMR) have also been used to clarify some of the features mentioned above.[35] The primary use of these polymers is as preceramic materials (Chapter 9)[33,36,37] which, when pyrolyzed, yield silicon nitride, Si_3N_4. The major general problems in this area are (i) use of a polymer that is tractable (soluble, meltable, or malleable),

(ii) generation of molecular weights high enough or polymers sufficiently cross-linked to hold their shape during the pyrolysis step, (iii) obtaining a high weight percent conversion to the ceramic, and (iv) avoidance of reactions that could lead to excessive porosity. A specific problem in the pyrolysis to silicon nitride is the necessity to remove all of the extraneous carbon atoms left over from the organic groups. These would affect the properties of the resultant silicon nitride product.[30,32,38]

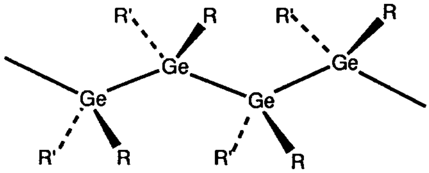
A variety of other ceramics are prepared by pyrolysis of preceramic polymers.[32,38] Some examples are silicon carbide, SC, tungsten carbide, WC, aluminum nitride, AlN, and titanium nitride, TiN. In some cases, these materials are obtained by simple pyrolysis in an inert atmosphere or under vacuum. In other cases a reactive atmosphere such as ammonia is needed to introduce some of the atoms required in the final product. Additional details are given in Chapter 9.

7.3 Polygermanes

Germanium falls directly below silicon in the periodic table and, as can be seen from **7.2** and **7.3**, the chain structure of the polygermanes is very similar to that of the polysilanes, discussed in Chapter 5. Not surprisingly, therefore, their properties are also very similar to those of the polysilanes.[39–42]



7.2



7.3

The earliest preparations of poly(organogermanes) yielded oligomers when phenyl R side groups were present. Some homopolymers with *n*-butyl side groups have been prepared, and a few copolymers having silane repeat units also are known. In these, a greater variety of side groups were employed. Monomers are typically prepared by Grignard reactions with, for example, $GeCl_4$. This is illustrated in reactions (6) and (7).

$$GeCl_4 + RMgX \rightarrow R_4Ge \tag{6}$$

$$R_4Ge + GeCl_4 \rightarrow R_2GeCl_2 \tag{7}$$

The resultant product, R_2GeCl_2, can then undergo a Wurtz coupling reaction in the presence of sodium, as in the preparation of the polysilanes discussed in Chapter 5. For this specific monomer, the molecular weights of the polymers may be quite high, with number-average values above a half million. Polydispersity indices are also rather high (around two or greater). When R_2GeBr_2 is used, the molecular weights have tended to be relatively low, under 10,000 g mol^{-1}, and the distributions seem to be narrow, with polydispersity indices of 1.1 to 1.3. The thermal stability is reported to be quite good.[42]

An alternative, recently reported route to polygermanes is the catalyzed dehydrogenative coupling of germanium hydrides.[40] Titanocene and zirconene derivatives are efficient catalysts, yielding high rates and high conversions. Dimethyltitanocene is particularly effective, but yields different products with different starting germanes. Specifically, primary germanes undergo coupling to give three-dimensional networks, presumably because of the reactivity of the backbone hydrogen atoms. Secondary germanes couple, apparently to form linear chains, but of rather low molecular weight.[40]

There has been a great deal of interest in the UV-visible spectroscopy of the polygermanes, particularly in comparison with the analogous chains that have silicon or tin backbones.[41,42] Both conventional and Raman spectroscopy have been employed. One interesting observation is that the symmetrically disubstituted poly(di-*n*-alkylgermanes) exhibit thermochromic transitions at temperatures below those of their polysilane analogues. Another is the conclusion that in poly(di-*n*-hexylgermane) the side chains adopt *trans*-planar conformations as in the polysilane counterpart. The two chains are also similar in that both backbones can, under certain circumstances, also adopt planar zig-zag conformations.

Intramolecular energy calculations have been made on polygermane chains, so additional information on their conformational preferences is available.[43] More specifically, molecular orbital calculations have been carried out as a function of rotations about the backbone bonds. For poly(dimethylgermane), the results predict a broad energy minimum located at the *trans* conformation, with two symmetrical, steeper and somewhat shallower minima near the usual *gauche* locations. The results are very similar to those for poly(dimethylsilane), except that the barriers are considerably lower.[43] This is apparently due to the fact that Ge–Ge bonds are approximately 0.30 Å longer than Si-Si bonds.[44–46] Unfortunately, no relevant experimental data might be used to test the validity of the calculations are available at the present time.

Like polysilanes, polygermanes can be decomposed and volatilized by exposure to radiation of the appropriate frequency. They have been considered for microlithographic applications.[42,43] Because they are more difficult and more expensive to prepare, and have no obvious advantages over polysilanes, they have not found much use to date in this type of application.

There has also been some interest in the preparation of poly(germanoxanes) with repeat units of the type [-GeR_2O-].[8]

7.4 Polymeric Sulfur and Selenium

7.4.1 Polymeric Sulfur

This polymer is obviously totally inorganic, and can be made directly by the ring-opening polymerization of rhombic sulfur, which consists of eight-membered sulfur rings.

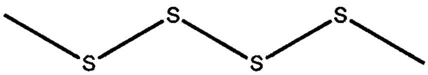
Rhombic sulfur is a brittle, crystalline solid at room temperature. Heating to 113 °C causes it to melt to a reddish-yellow liquid of relatively low viscosity. Above approximately 160 °C, the viscosity increases dramatically because of the free-radical polymerization of the cyclic molecules into long, linear chains.[6,8,14,30,47–51] At this point, a degree of polymerization of approximately 10^5 is obtained. If the temperature is increased to above approximately 175 °C, depolymerization occurs, as evidenced by a decreasing viscosity. A similar type of depolymerization occurs with the polysiloxanes discussed in Chapter 4. In thermodynamic terms, the negative $-T\Delta S$ term overcomes the positive ΔH term for chain depolymerization. (The temperature at which the two terms are just equal to one another is called the "ceiling temperature" for the polymerization.)

In any case, if this polymerized form of elemental sulfur is quenched (cooled rapidly), it becomes a solid. This solid is glassy at very low temperatures, but becomes highly elastomeric above its glass-transition temperature of approximately –30 °C.[6,8,14,30] The situation is complicated by the presence of unpolymerized S_8 molecules which would certainly act as plasticizers. So far, attempts to cross-link the elastomeric form into a network structure suitable for stress–strain measurements have not been successful. The polymer is unstable at room temperature, gradually crystallizing, and eventually reverting entirely to the S_8 cyclics.

The ability of sulfur to form chains is also important in the sulfur vulcanization of diene elastomers such as natural rubber. In this case, strings of sulfur atoms of varying length form the cross-links that tie one chain to another. In this sense, they can be thought of as the short chains of a short chain–long chain "bimodal" network, as was described in Chapter 4.

Cyclic Se_8 molecules have also been polymerized by heating.[30] These chains are described in the following section.

Sulfur chains are fascinating since their structure is the simplest possible: all the chain atoms are identical and bear no substituents or side chains.[52–54] A sketch of the chain is shown in **7.4**. The bond lengths are 2.06 Å, the bond angles are 106°, and the rotational states are located at ±90°. The rotational barrier is approximately 10 kcal mol^{-1} and the van der Waals radius of the sulfur atom is 1.80 Å. The sulfur chain in the crystalline state is a helix in which all of the rotational angles are of the same sign and are 96°, very close to the value expected from the minimum conformational energy.[52]



7.4

The distances between neighboring atoms in all conformations give rise to favorable (attractive) interactions. These attractions are particularly strong in the two most compact conformational pairs, ±90°, ±90°, and in none of the conformations are there severe steric overlaps. These circumstances are very different from those in typical organic polymers. These conformational preferences should make sulfur chains extremely compact, with very small unperturbed dimensions. Conformational analyses, in fact, indicate that the characteristic ratio of polymeric sulfur should be less than unity (which is the "freely jointed" value).[52]

Because of the instability of sulfur chains it has not yet been possible to obtain an experimental value of the characteristic ratio with which to test the theoretical predictions. However, experimental values of the dipole moments are available for alkyl-terminated chains of 2, 3, and 4 sulfur atoms. Comparison of these experimental results with values calculated using the same conformational analyses does give good agreement, thus lending support to the proposed model.[52–54] An accurate experimental value is known for the entropy of cyclization of polymeric sulfur back to the cyclic octomer. Use of the conformational information mentioned, in an appropriate cyclization theory does give a good account of this entropy change.[55] Additional calculated results have been carried out to elucidate the conformational preferences of a variety of small molecules that contain S–S bonds, the relative stabilities of cyclic sulfur molecules of varying ring size, and the self-depression of the melting point of elemental atomic sulfur arising from the presence of sulfur cyclics.

It is also possible to prepare sulfanes, RS_xR, which are relatively long chains of sulfur capped with R end groups.[7] In one synthesis, a thiosulfate solution is acidified with a strong acid, to yield a hydrogen-terminated sulfur chain. Other end units such as alkyl groups, aryl groups, halogens, and mono- and di-sulfonic acids are also known. Some polymers of this type have been characterized and used in applications that involve coating additives.

A variety of copolymers have been synthesized by the direct copolymerization of S_8 with other comonomers.[56] For example, S_8 undergoes an equilibrium copolymerization with Se_8, as shown in reaction (8):

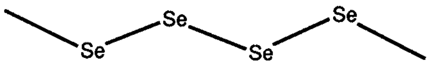
$$S_8 + Se_8 \rightarrow [\text{-}S_xSe_y\text{-}] + S_{8-x}Se_x \tag{8}$$

Cyclic species $S_{8-x}Se_x$ are formed as well as the linear copolymer $[\text{-}S_xSe_y\text{-}]$. The reaction of sulfur with arsenic is more complicated than can be explained by this simple difunctional equilibrium. In particular, the trifunctional As atoms give rise to a three dimensional network structure.[56]

Small amounts of phosphorous can be used to vulcanize polymeric sulfur. Larger amounts yield the P_4S_4 "bird-cage" molecules mentioned in Section 6.2 on "Other Phosphorous-Containing Polymers" in Chapter 6, together with phosphorous-sulfur copolymers. The copolymers are hydrolytically unstable.[56]

7.4.2 Polymeric Selenium

Selenium exists in the form of a cyclic octomer, which can rearrange to long, polymeric chains. As can be seen from **7.5**, the selenium chain is very similar to that of sulfur. The bond angles are 104°, essentially the same as those in polymeric sulfur, and rotational states are also thought to occur at the same angles, ±90°.[52–54] However, the skeletal



7.5

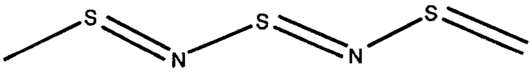
bonds are 2.34 Å long, which is longer than the S-S bonds in the polymeric sulfur chain. This long bond length more than offsets the repulsions expected from the increase in van der Waals radius (to 1.90 Å) and this chain should be even more flexible. If so, it might have a lower glass-transition temperature than polymeric sulfur. Actually, this is hard to predict purely on the basis of bond flexibility, since interchain interactions are generally also important (or "plasticizers" simply would not work!).

The crystalline state configuration of polymeric selenium is a helix in which all the rotational angles are of the same sign with a value of ±78°. This is fairly close to the expected value of ±90°.[52] The barrier to rotation about the Se-Se bond is thought to be roughly the same as that about S-S bonds. No reliable experimental results are available on the statistical properties of these chains. Some values of the glass-transition temperature of polymeric selenium have been reported[15] and these could at least provide a measure of the dynamic flexibility of the chains. However, these results are probably compromised by the presence of cyclic selenium molecules that act as plasticizer.

Not surprisingly, tellurium forms some polymeric materials analogous to those formed by sulfur and selenium.[15,28]

7.5 Other Sulfur-Containing Polymers

The most important polymer in this category is probably poly(sulfur nitride), also known as polythiazyl,[12,56–60] which is shown schematically in **7.6**. The synthesis of this sulfur-nitrogen polymer $(SN)_x$ starts from the eight-membered cyclic tetramer, $[SN]_4$. The tetramer itself can be prepared by the reaction of ammonia with elemental sulfur, sulfur fluorides, or sulfur chloride. It is a crystalline solid with a sublimation temperature of 178 °C. It is also prone to detonation. In the vapor state it can be catalytically converted (with metallic silver at elevated temperatures) to the cyclic dimer which, in turn, polymerizes in the solid state to the $[SN]_x$ polymer.[12,56,57] Several days are normally required for the polymerization. The mechanism is thought to involve ring cleavage, with the two resulting radicals combining with the nearest neighbors bracketing them in the crystal structure.[30,61] Because a sublimation step is involved in the polymerization process, there has been considerable interest in epitaxial chain growth (where the polymerization occurs on surfaces of known and controlled structure). In practice, the polymer depolymerizes at approximately 150 °C to a gaseous S_4N_4 isomer. When this isomer in the vapor state comes into contact with the desired surface at a lower temperature, it spontaneously repolymerizes to give the $(SN)_x$ film.[12]



7.6

The polymer is highly crystalline, which facilitates structure analysis, but has thwarted attempts to measure its properties in solution. The preparation of single crystals has been useful with regard to the characterization of its structure. Its crystal structure is known, but not much is known about typical molecular weights. The S–N and N–S bonds are essentially identical in length, with a bond order that is intermediate

between those expected for normal single and double bonds.[12] Conformationally, the chains are in nearly planar, crank-shaft arrangements. Electron microscopy shows the crystals to be composed of layers of fibers parallel to the long axis of the crystal. They are soft and malleable, and have a golden metallic luster. They conduct electricity like a metal down to very low temperatures, with highly anisotropic conductivity in the case of the oriented chains.[30] The conductivity increases by several orders of magnitude as the temperature is decreased from room temperature to a few degrees Kelvin. At 0.26 K, $(SN)_x$ becomes a superconductor. The electrical conductivity is thought to require both the charge delocalization that is possible along the chains, and the highly ordered chain arrangements present in the crystalline state. Brominated polythiazyl chains are also being studied in this regard.[61] They are prepared by direct bromination of the polymer at ambient temperatures, and have the composition $(SNBr_y)_x$, where y is approximately 0.4.

The chains were found to be stable in an inert atmosphere, but decomposed above approximately 140 °C, into sulfur, nitrogen and low-molecular-weight sulfur-nitrogen molecules. Unfortunately the polymer oxidizes easily, which may cause loss of some of its most interesting properties.[30] Its insolubility, and failure to melt without decomposition, greatly complicate its processing into fibers or films. However, it has been used extensively as an electrode material. A final difficulty is the explosive nature of many sulfur-nitrogen compounds. The situation could possibly be simplified if sulfur-nitrogen chains could be prepared with substituents linked to the S atoms.[14] These and other problems merit additional investigation.

For example, there is considerable interest in the preparation of sulfur-nitrogen polymers that have organic substituents on the sulfur atoms.[56] This could help alleviate the intractability problem mentioned, and could also give rise to a series of polymers that parallel the phosphazenes in their structural variability. A series of polymers with S–N backbones of this type has been prepared, but with oxygen atoms as some of the substituents. The basic structure has the repeat unit –RS(=O)(N)– or –FS(=O)(N)–, but they have not yet been studied in detail. The fluorine-containing polymer, however, is known to be a tough elastomer which is unaffected by water, acids, or bases up to 100 °C.[7]

Some of the most useful series of polymers in this category are the polysulfides.[62] Their repeat units consist of a variable number of skeletal sulfur atoms separated by organic groups. The organic groups can be either hydrocarbon sequences, as in $\text{-(CH}_2)_m\text{S}_n\text{-}$, ether moieties, as in $\text{-(CH}_2)_m\text{OS}_n\text{-}$, or units such as in $\text{-(CH}_2)_m\text{OCH}_2\text{OS}_n\text{-}$. In these notations, m and n are typically 2–4. Early materials of this type were high-molecular-weight solid elastomers called "Thiokols," but the most important products today are lower molecular weight liquids with mercaptan end groups that permit them to be converted into an elastomer in situ. They have excellent radiation resistance, and also have very good adhesion to some metals and to glass. This latter characteristic makes them particularly useful as adhesives, sealants, and coatings.[62] Mercaptan end groups have also been extensively used for tethering chains onto gold surfaces in a variety of supramolecular syntheses.[63–67]

Because of the inorganic nature inherent in the strings of sulfur atoms in their backbones, these polymers have excellent resistance to hydrocarbon solvents that can swell common hydrocarbon elastomers. They also have good resistance to moisture, oxygen, and ozone, good weatherability, and better-than-average low temperature properties.[62]

In general, higher sulfur contents give better properties of this type. The sequences of skeletal sulfur atoms also present problems, however, as can be anticipated from the polymerization-reorganization behavior mentioned earlier with regard to polymeric sulfur itself. Because of this problem, the polysulfide elastomers have relatively poor high-temperature stability and pronounced compression set (permanent deformation or "creep" under stress). The presence of the skeletal sulfur atoms and the sulfur atoms in the mercaptan end groups can cause odor problems as well, although most of this has been blamed on trace impurities.

Materials prepared with liquid-like properties as mentioned above have molecular weights of only a few thousand. A variety of chemical curing agents are used to cross-link them, with PbO_2 and chromates being good examples.[62]

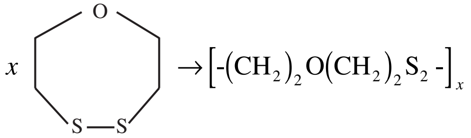
These polymers are typically prepared by reaction of sodium polysulfide with a formal. *Bis*(2-chloroethylformal) is commonly used, but some *tri*functional chlorinated hydrocarbon with its associated higher functionality is typically also added to promote branching. The sodium polysulfide is usually made by the direct reaction of sodium hydroxide with sulfur at temperatures near 120 °C, as shown in reaction (9):[62]

$$6\text{NaOH} + 2(x+1)\text{S} \rightarrow 2\text{Na}_2\text{S}_x + \text{Na-(S)}_x\text{-Na} + 3\text{H}_2\text{O} \tag{9}$$

The polysulfide then reacts by a condensation polymerization with the difunctional and trifunctional chloro compounds. It is also possible to react cyclic S_8 with a mercaptan-capped molecule or dithiol in a condensation reaction in the presence of a basic catalyst. An example is the reaction with ethanedithiol (reaction (10)):[56]

$$x\text{HS}(\text{CH}_2)_2\text{SH} + (xy/8)\text{S}_8 \rightarrow [\text{-}(\text{CH}_2)_2\text{S}_y\text{-}] + \text{H}_2\text{S} \tag{10}$$

Another preparative technique involves the ring-opening polymerization of cyclic polysulfides.[56] For example, 1-oxa-4,5-dithiacycloheptane polymerizes very rapidly at room temperature when treated with an aqueous sulfide (reaction (11)):



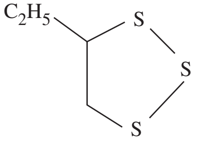
(11)

The related monomer, 1,3-dioxa-6,7-dithiacyclononane, can be polymerized in the same manner. A variety of catalysts, both anionic and cationic are effective. Similarly, 1,2-dithiacycloalkanes can be polymerized with traces of $AlCl_3$ (reaction (12)):

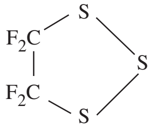
$$x\left(\begin{smallmatrix}(\text{CH}_2)_m\\ \text{S–S}\end{smallmatrix}\right) \xrightarrow{\text{AlCl}_3} [\text{-}(\text{CH}_2)_m\text{S}_2\text{-}]_x \tag{12}$$

Polymers that have several values of m in the range 3–13 have been prepared. The estimated ring strain energies of these monomers show a good correlation with measured heats of polymerization.

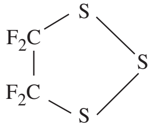
As shown in reaction (13), some of the corresponding cyclic trisulfides can also be polymerized, often to high-molecular-weight materials. For example, 1-ethyl-2,3,4,-trithiacyclopentane can be polymerized[56]

x  $[\text{-CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{S}_3\text{-}]_x$ (13)

to produce an elastomer that has a molecular weight of several hundred thousand. Another related polymerization involves cyclic trithiaderivatives of tetrafluoroethylene, prepared by sulfuration of the olefin in the gas phase (reaction (14)):[56]

$$x\text{F}_2\text{C} = \text{CF}_2 + (3n/8)\text{S}_8 \rightarrow x$$  (14)

This monomer can then be polymerized in the presence of base

x  $\rightarrow [\text{-CF}_2\text{CF}_2\text{S}_3\text{-}]_x$ (15)

to yield a crystalline polymer of relatively high molecular weight (reaction (15)). The sulfuration method can also be used to prepare *ortho*-fused 1,2,3-trithia derivatives of norbornene, and di- and tricyclopentadiene, which can then be polymerized anionically to the corresponding polytrisulfides.[56]

Only a few examples are known of polymerizations to cyclic species that have more than three consecutive S atoms in the repeat unit. One example is poly(tetrafluoroethylene tetrasulfide), which can be prepared in a manner similar to that shown in reaction (15).[56]

The cyclic S_8 monomer may be copolymerized directly with unsaturated monomers.[56] This reaction is illustrated by the equation:

$$x\text{CH}_2\text{=CR}'\text{R}'' + (xy/8)\,\text{S}_8 \rightarrow [-\text{CH}_2\text{CR}'\text{R}''\text{S}_y-] \qquad (16)$$

Examples of organic comonomers studied to date are methyl acrylate, methyl methacrylate, and vinyl acetate. The number of S atoms thus introduced into the repeat unit is highly variable, and changes with the nature of the diene, the temperature, feed composition and method of initiation. However, typical values are generally in the range of 3–8.[56] The reaction of sulfur with the double bonds in diene elastomers, such as natural rubber and *cis*-1,4-butadiene, also falls into this category. Not surprisingly, similar reactions occur between S_8 and small-molecule dienes. Also, copolymerizations between S_8 and aryl alkynes have been reported, with an example of the organic comonomer being phenylacetylene.[56]

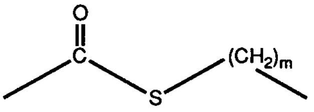
Cyclic S_8 can also be copolymerized with cyclic mono- and polysulfides such as thiiranes and trithiolanes.[56] The result is a polysulfide with an augmented number of S atoms in the repeat unit.

S-S bonds are important in biological polymers. For example, one of the ways in which proteins are held in very precisely controlled arrangements is through disulfide linkages, and this is particularly important in enzymes and antibodies.[56] Not surprisingly, a great deal of interest exists in carrying out reactions in the laboratory that simulate the function of these biopolymers. Disulfide spacers have also been used to attach biologically active groups to a variety of polymer backbones.

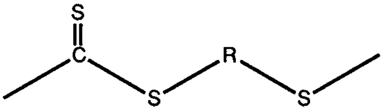
Some general comments can also be made with regard to the physical properties of some of these polymers. For example, the properties of polysulfides generally show a very strong dependence on composition.[62] The glass-transition temperature T_g is of particular interest. Specifically, polysulfides in which the organic groups are a simple -$(CH_2)_m$- hydrocarbon sequence have relatively high values of T_g, typically around –25 °C. If, the organic chain units are ether groups, -$(CH_2)_m$O-, the values of T_g are lower, typically around –50 °C.[44–46,62] This is consistent with the known increase in flexibility that results from the presence of dicoordinate oxygen atoms.[52] The formal group, -$(CH_2)_m OCH_2O$-, would thus be expected to introduce even more flexibility, and this is found to be the case. These polymers show the lowest values of T_g in this series, around –75 °C. Lengthening of the hydrocarbon sequences tends to decrease the T_g, which is consistent with the very low glass-transition temperature (probably around –125 °C), found for polyethylene.[44–46] On the other hand, lengthening of the sulfur sequences tends to increase T_g. This is also to be expected, in view of the relatively high value of T_g for polymeric sulfur (–30 °C).

The tendency for crystallization also varies with structure, in particular with the lengths and nature of the organic sequences. Crystallization during storage at low temperatures can cause the elastomer to harden, and to become less processable. Such crystallization can be avoided entirely by making the chain structure highly irregular, by using a mixture of the organic reactants instead of a single species. One such mixture consists of butyl formal and butyl ether.[62]

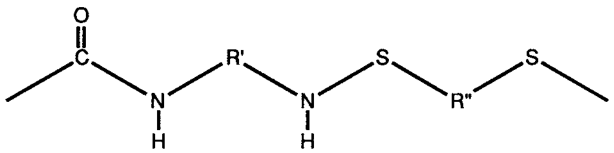
A number of sulfur-containing polymers do not contain S–S bonds, but are simply analogues of the corresponding oxygen-containing polymers long known in classical organic polymer chemistry. Some examples are poly(thioesters), poly(thiocarbonates), and poly (thiocarbamates). Their structures are shown in **7.7** through **7.9**. Poly(thioethers) that have structures [-$(CH_2)_m$S-]$_x$ also exist. These are analogues of the much-studied polyalkylene-oxides [-$(CH)_m$O-]$_x$.[52–54] None of the polymers in these series possess much inorganic character, and are best considered as parts of the organic series, as mentioned earlier.



7.7



7.8

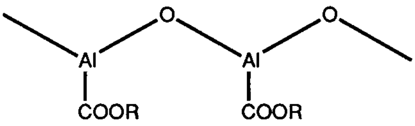


7.9

7.6 Aluminum-Containing Polymers

The reactions of metallic aluminum with an alcohol can generate oligomeric structures that contain Al-O bonds. Of greater interest, however, is the reaction of $AlCl_3$ with the salt of an organic acid to give aluminum dialkanoates. These have chain-like structures, and a range of molecular weights. These polymers are used as "drag-reduction" agents either in water or organic fluids. Drag reduction agents reduce the resistance of fluid flow through pipes. This is very useful in fire fighting, oil pumping, and so on.

The reactions of trialkylaluminum reagents with an organic acid can yield a poly(acyloxyaloxane) or poly(aluminoxane) with the structure shown in **7.10**. Although the molecular weights are quite low, and the chains may have considerable branching and cross-linking,[7] the polymers can be melt spun into fibers, which themselves can be pyrolyzed to alumina, Al_2O_3. Other applications include their use as drying or gelling agents, and as lubricants.

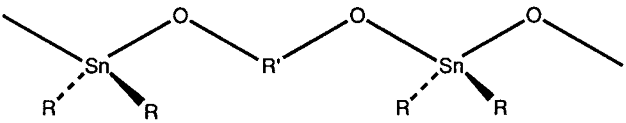


7.10

Another type of polymer in this category is similar to **7.10**, but in which the O atoms are replaced by NH groups. These aluminum-nitrogen chains are thermally and hydrolytically unstable, and are sensitive to acids and bases.[7] However, this polymer can also be drawn into fibers, which can be converted to aluminum nitride, AlN, in the presence of ammonia.[68]

7.7 Tin-Containing Polymers

Although there are a variety of polymers in this category,[69–71] most polymers with tin atoms in the chain backbone are represented by the stannoxane structure **7.11**,

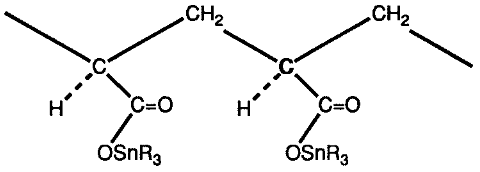


7.11

where R represents a variety of organic groups. They are typically prepared by an interfacial polymerization between a diorganotin dihalide and a difunctional organic molecule. The nitrogen analogues, in which NH groups replace the O atoms in this structure, have also been prepared. The most notable characteristic of this class of polymers is their good thermal stability.

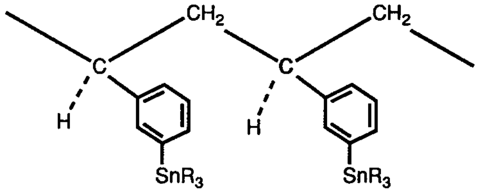
A variety of oligomers with novel "drum" and "ladder" structures have also been prepared. They have the formulas $[R'Sn(O)O_2CR]_6$ and $[(R'Sn(O)O_2CR)_2R'Sn(O_2CR)_3]_2$, and contain four- and six-membered rings. They can be synthesized by the reaction of stannoic acid with a carboxylic acid, but the reaction of $RSnCl_3$ with the silver salt of a carboxylic acid can also be used. If diphenylphosphinic acid or dicyclohexylphosphinic acid is used instead of the carboxylic acid, oxygen-capped clusters or cubic and butterfly structures are obtained.[69]

Also of interest are polymers that have tin atoms in their side chains. Typically these polymers consist of vinyl chains with $-COOSnR_3$ side groups, as illustrated in **7.12**. Such side groups have also been much used in copolymers, for example in poly(tri-*n*-butyltin methacrylate/methyl methacrylate).[70] These materials have been used as anti-fouling paints on ships and off-shore oil platforms. They are believed to work by hydrolysis to liberate Sn ions, which deter the growth of marine organisms. The R_3SnOH formed in the hydrolysis and some of its degradation products are tenaciously adsorbed by clays. However, the tin ions can have considerable toxicity and may accumulate in bodies of water when ships are in harbor for extended periods of time. The use of tin polymers for this application is now being discouraged.



7.12

A new type of polymer with tin atoms in the side groups is polystyrene with $-R_3Sn$ groups attached to the phenyl groups, as shown in **7.13**. Because these polymers contain no O-Sn bonds they are generally less hydrolyzable, and therefore generate less of a problem in the environment. It is thought that their hydrolyzability can be increased, if desired, by attaching bulky R groups to the tin atoms. This raises the possibility of fine-tuning this important property.[72]



7.13

7.8 Arsenic-Containing Polymers

Arsenic occurs in some polymeric chains, that are possibly ladder-like in structure. The backbones are described as being made up entirely of arsenic atoms, and the molecules have the empirical formula $[AsCH_3]_x$.[16,73] This polymer is prepared by the reaction of iodine with $(AsCH_3)_5$, but the range of colors and physical forms obtained suggest that the material may not be uniform in composition. Antimony is also thought to form ladder structures similar to those described for arsenic. The polymers are formed by the reaction of alkylstilbenes, $RSbH_2$, with a halogen source.[16,73] Bismuth forms very few compounds of any type with Bi-Bi bonds, although there has been a report of a polymer with the structure $(C_6H_5Bi)_x$.[16,73]

7.9 Metal Coordination Polymers

7.9.1 A Survey of Typical Structures

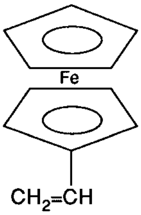
In this class of polymers, coordination occurs between an organic group in the polymer and a metal atom. This coordination may result in the metal atom being attached as a side group or part of a side group, or as an integral part of the chain backbone.[74–78]

A simple example of the first type of polymer is poly(vinyl pyridine), $[-CH_2CH(C_5H_4N)-]_x$, where the nitrogen atom in the $-C_5H_4N$ side group has unpaired electrons available for coordination. Another example would be an ionic side chain, which could coordinate with a metal cation.

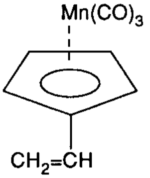
Much more research has been carried out with polymers in which the coordinated metal atom is part of the chain backbone. Typically, the metal atoms are copper, nickel, and cobalt. Oxygen atoms or carbon atoms adjacent to the metal atom provide the electrons required for the coordinate bond.[30] Polymers of this type are often rather intractable, for a variety of reasons. Specifically, insolubility can be a problem for species with moderate molecular weights. Also, coordination between chains can cause aggregation, and ligand-exchange reactions with small molecules such as solvents can cause chain scission. However, in some favorable cases, the intramolecular coordination is sufficiently strong for the polymer to be processed by the usual techniques such as spinning into fibers or extrusion into films.[30]

In other examples, compounds in which a metal atom is already coordinated in a molecule can be used as a comonomer in an addition polymerization. Two examples involve the ferrocenes discussed in Chapter 6. The vinyl ferrocene molecule is shown in **7.14**, and a similar vinyl manganese complex in **7.15**.[30] An alternative approach involves condensation polymerization. For example, if the R group in the ferrocene unit shown in **7.16** contains a hydroxyl group, it can be copolymerized with a diacid chloride. If it is an acid chloride, it can be copolymerized with a diamine. (This type of polymer is called a heteroannular chain; if only one of the rings in the repeat unit is in the backbone, the polymer is called homoannular.)[7] Similarly, the titanium complex shown in **7.17** is copolymerized with diacids or diols.[30] Numerous other examples involving ferrocenes are discussed in Chapter 6.

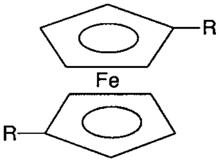
Some metals form coordination polymers with sulfur that have a semi-ladder structure. One series are the bisdithiocarbamate polymers, which have the typical structure shown



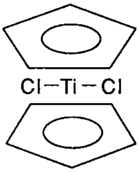
7.14



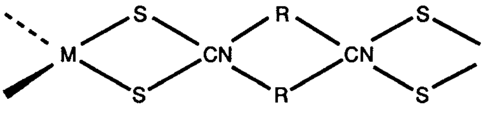
7.15



7.16



7.17



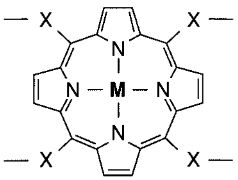
7.18

in **7.18**. The tetrahedral zinc polymer is called "Zineb" and the manganese one is called "Maneb." Both are water-soluble fungicides. Other ladder-type structures occur in zirconium tetrasalicyclidene-1,2,4,5-tetraaminobenzene polymer, and in *bis*(5,7-dichloroquinolinolato)quinoxaline-5,8-diolatotungsten(IV) polymer.[77]

Mercury, like zinc, appears in some chain-like structures, but apparently only in combination with other metals such as As, Sb, Nb, and Ta. Some of these have the characteristics of metallic conductors.[15] Rather high molecular weights have been obtained in the preparation of 6-coordinate cobalt (III) chelate polymers with acetylacetonato and leucinato ligands, 7-coordinate dioxouranium-(VI) dicarboxylate polymers, and 8-coordinate zirconium (IV) polymers with Schiff-base ligands.[77]

7.9.2 Metalloporphyrin Polymers

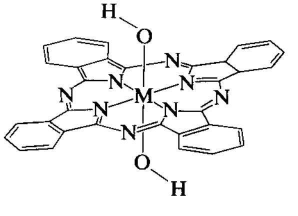
In the most important series of polymers of this type, the metallotetraphenylporphyrins, a metalloporphyrin ring bears four substituted phenylene groups X, as is shown in **7.19**. The metals M in the structure are typically iron, cobalt, or nickel cations, and the substituents on the phenylene groups include -NH_2, -NR_2, and -OH. These polymers are generally insoluble. Some have been prepared by electro-oxidative polymerizations in the form of electroactive films on electrode surfaces.[79] The cobalt-metallated polymer is of particular interest since it is an electrocatalyst for the reduction of dioxygen. Films of poly(trisbipyridine)-metal complexes also have interesting electrochemical properties, in particular electrochromism and electrical conductivity.[78] The closely related polymer, poly(2-vinylpyridine), also forms metal complexes, for example with copper(II) chloride.[80]



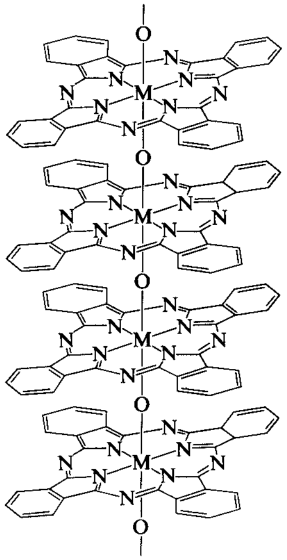
7.19

7.9.3 Cofacial Phthalocyanine Polymers

The phthalocyanine group is structurally related to the porphyrin group discussed in the preceding section. It consists of a series of interconnected rings containing nitrogen atoms, some of which face inward in such a way that they can complex very strongly with metal or metalloid atoms attracted to their unpaired electrons. This is illustrated in **7.20**, where typical M atoms are Si, Ge, or Sn. Dehydration of the "monomer" complexes induces condensation polymerization to yield a stacked "shish kebab" chain structure of the type shown in **7.21**. The backbone consists of the M atoms alternating



7.20



7.21

with divalent atoms such as oxygen, as is shown in **7.21**.[81–85] The degrees of polymerization can be a hundred, or higher. Such polymers have excellent chemical and thermal stability. They can, for example, be dissolved in strong acids, frequently without degradation. Such solutions are important, possibly because protonation of some of the basic nitrogen atoms converts the chains into polyelectrolytes with sufficient coulombic repulsions to keep them dispersed long enough for processing. In this way it is possible to prepare fibers. As described below, these can become electrically conducting when treated with a dopant such as iodine.[30] They may also have interesting magnetic and electro-optical properties. With regard to electrical conductivity, these materials have the two major characteristics for producing a conducting arrangement of polymeric chains.[81–84] These are the presence of partially filled valence shells in the molecules, and the orientation of the rings into closely packed arrays, each ring with similar crystallographic and electronic environments. Thus the charge-carrying molecular subunits are covalently linked in a long chain, with cofacial orientations. The chains are relatively rigid, and may be stiff enough to spontaneously form anisotropic liquid-crystalline phases similar to those used to spin aramid fibers such as Kevlar. It has been found that solutions of the siloxane-type cofacial polymer can be extruded alone or in combination with Kevlar to form strong oriented fibers.[81–84] Doping of these fibers can be carried out either before or after the spinning process, to yield air-stable, electrically conducting fibers.

7.10 Other Organometallic Species for Sol-Gel Processes

The sol-gel process described in Chapters 8 and 9 often involves the use of organosilicates (alkoxysilanes), but a variety of other organometallic substances may be used for

this purpose.[36,86–102] For example, titanates can be hydrolyzed, condensed, and polymerized in a series of steps that ultimately lead to titania. Aluminates yield alumina, borates give boria,[92] zirconates give zirconia, and so on. The possible variety of such reactions seems almost endless, and only a small fraction have been investigated to date. As mentioned in the discussion of silane-silica systems, much of this field lies on the fringes of inorganic polymer chemistry, and represents an important interface with the area of high-performance ceramics.

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8

Inorganic-Organic Hybrid Composites

8.1 Sol-Gel Ceramics

A relatively new area that involves silicon-containing materials is the synthesis of "ultrastructure" materials, that is materials in which structure can be controlled at the level of around 100 Å. An example of such a synthesis is the "sol-gel" hydrolysis of alkoxysilanes (organosilicates) to give silica, SiO_2.[1–14] The reaction is complicated, involving polymerization and branching, but a typical overall reaction may be written

$$Si(OR)_4 + 2H_2O \rightarrow SiO_2 + 4ROH \quad (1)$$

where the $Si(OR)_4$ organometallic species is typically tetraethoxysilane (tetraethylorthosilicate) (TEOS, with R being C_2H_5). In this application, the precursor compound is hydrolyzed and then condensed to polymeric chains, the chains become more and more branched, and finally a continuous highly swollen gel is formed. It is first dried at moderately low temperatures to remove volatile species, and then is fired into a porous ceramic object. It can then be densified, if desired, and machined into a final ceramic part. Not surprisingly, the production of ceramics by this novel route has generated a great deal of interest. Its advantages, over the usual "heat-and-beat" (e.g., sintering) approach to ceramics, is (i) the higher purity of the starting materials, (ii) the relatively low temperatures required, (iii) the possibility of controlling the ultrastructure of the ceramic (to reduce the number of microscopic flaws that lead to brittleness), (iv) the ease with which ceramic coatings can be formed, and (v) the ease with which ceramic *alloys* can be prepared (for example, by hydrolyzing solutions of both silicates and titanates).

This approach has been used to form ceramic-like phases in a wide variety of polymers. The one which has been studied the most in this regard is poly(dimethylsiloxane) (PDMS), the semi-inorganic polymer featured extensively in Chapter 4. This is due to PDMS being in the class of relatively weak elastomers most in need of reinforcement, and being capable of easily absorbing the precursor materials generally used in the sol-gel process.

8.2 Fillers in Elastomers

8.2.1 Generation of Approximately Spherical Particles

The same hydrolyses can be carried out within a polymeric matrix to generate *particles* of the ceramic material, typically with an average diameter of a few hundred angstroms.[12–17] The polymer typically has end groups, such as hydroxyls, that can participate in the hydrolysis-condensation reactions.[18–20] Such end groups provide better bonding between the two rather disparate phases, but bonding agents may also be introduced for this purpose.[21] Considerable reinforcement of elastomers, including those prepared from PDMS, can be achieved in this way. This method for introducing reinforcing particles has a number of advantages over the conventional approach in which separately prepared filler particles are blended into the uncross-linked elastomer before its vulcanization.[22–24] This ex-situ time-honored technique is difficult to control because the filler particles are generally badly agglomerated and the polymer is typically of high enough molecular weight to make the viscosity of the mixture exceedingly high. Thus, the blending technique is energy intensive and time consuming, and frequently not entirely successful.

In contrast, because of the nature of the in situ precipitation, the particles are well dispersed and are essentially unagglomerated (as demonstrated by electron microscopy). The mechanism for their growth seems to involve simple homogeneous nucleation, and since the particles are separated by polymer, they do not have the opportunity to coalesce. A typical transmission electron micrograph of such a filled material is shown in Figure 8.1.[25] The particles are relatively monodisperse, with most of them having diameters in the range of 100–200 Å. The growth of the particles in from the surface of a PDMS sample can be followed by nuclear magnetic resonance (NMR), as is illustrated in Figure 8.2.[26] This approach utilized ^{1}H and ^{29}Si magic-angle spinning, with two-dimensional Fourier transform spin-echo techniques. It is based on the study of ^{1}H spin-spin (T_2) relaxation times of the protons in the PDMS polymer as they were being constrained by silica-like material being generated in their vicinities. For testing purposes, this composite was intentionally made to be inhomogeneous, with much larger amounts of silica being on the surface. The sample employed was cylindrical in shape, with a height of approximately 1 cm and a diameter of approximately 2 cm. The dark rim at the edge of the sample seen in the figure presumably indicates a reduced mobility of the network chains due to the presence of the silica. Its change in location with time can help characterize the movement of the reaction front into the sample. This technique is obviously non-destructive but if the sample can be sacrificed, then slices taken from it can be further studied in a gradient column with regard to density, by electron microscopy,[27] or by X-ray or neutron scattering.

The remainder of this section provides some additional details on the use of this technique.[16,18] In particular, the methods can be quite general, in that a variety of other

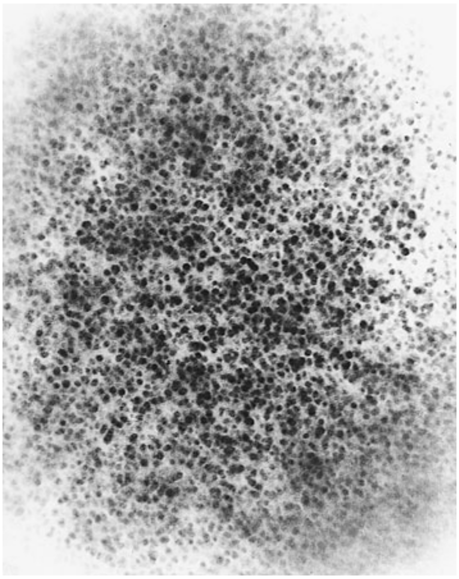

Figure 8.1 Transmission electron micrograph of a PDMS network containing 34.4 wt % in situ precipitated silica particles.[25] The average particle diameter is 150 Å. Reproduced by permission of John Wiley and Sons.

precursor materials can be hydrolyzed, photolyzed, or thermolyzed to give reinforcing, ceramic-type particles. For example, titanates can be hydrolyzed to titania, aluminates hydrolyzed to alumina, and metal carbonyls photolyzed or thermolyzed to metals or metal oxides. (Some of the metal or metal oxide particles could be particularly interesting if they can be manipulated with an external magnetic field during the curing process.) It is also possible to polymerize conducting polymers such as polyaniline within polysiloxane matrices.[28] Also, the method can be used in a variety of polymers (organic as well as inorganic, non-elastomeric as well as elastomeric). Even a non-polar,

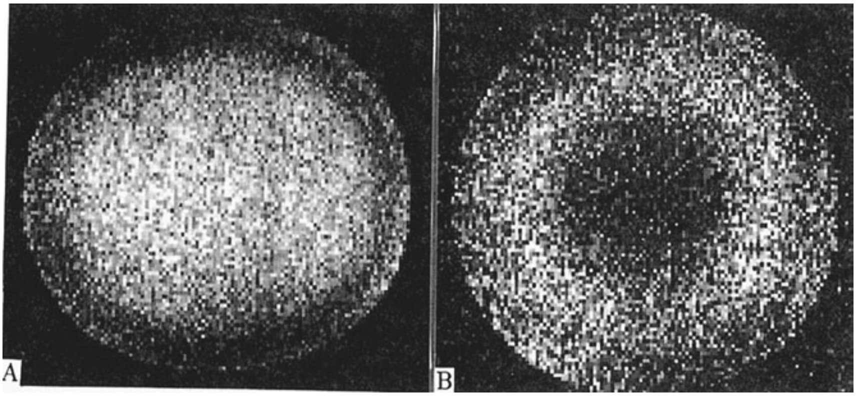

Figure 8.2 ^1H NMR images of a SiO_2-PDMS elastomeric sample obtained with a two-dimensional spin echo sequence having an echo time of 3.3 ms (portion A) and 22.7 ms (portion B).[26] The view is down the axis, and the resolution is 128X by 128X pixels of 211 and 236 mm, respectively (in A), and 211 mm in both axes (in B).

purely hydrocarbon polymer can be reinforced in this way, provided the precursor material is chosen so as to have significant miscibility with it. The technique is also general in that it is much used in an entirely different area by the ceramists, namely the sol-gel approach to generating purely ceramic objects, or monoliths, as mentioned above.

A variety of catalysts work well in the typical hydrolyses reactions used, including acids, bases, and salts.[29] Basic catalysts give precipitated phases that are generally well-defined particles, whereas the acidic catalysts give more poorly defined, diffuse particles.[4,30] In some cases, particles are not formed at all, and bicontinuous (interpenetrating) phases result.[17,31]

These sol-gel polymer reactions can be carried out in three ways.[16,18] In the first, the polymer is cross-linked and then swelled with the organometallic reagent, which is then hydrolyzed in situ. In the second, hydroxyl-terminated chains are blended with enough of the organometallic compound (TEOS) to both end-link them and generate silica by the hydrolysis reaction. Thus, curing and filling take place simultaneously, in a one-step procedure. In the third technique, TEOS is blended into a polymer that has end groups (e.g., vinyl units) that are unreactive under hydrolysis conditions. The silica is then formed in the usual manner (equation (1)), and the mixture is dried. The resultant slurry of polymer and silica is stable and can be cross-linked at a later time using any of the standard techniques, including peroxide cures, vinyl-silane coupling, or irradiation. It is also possible to generate the catalyst and other reactants themselves in situ, to give composites of unusually high transparency.[32]

Interesting "aging" effects are frequently observed in these systems. If the precipitated particles are left in contact with the hydrolysis catalyst and water they appear to reorganize, so that their surfaces become better defined and their sizes become more uniform.[15] The process seems quite analogous to the "Ostwald ripening"[33] much studied by colloid chemists.

The reinforcing ability of such in situ generated particles has been amply demonstrated for a variety of deformations, including uniaxial extension (simple elongation), biaxial extension (compression), shear, and torsion.[16,18,34,35] In the case of uniaxial extension, the modulus $[f^*]$ frequently increases by more than an order of magnitude, with the isotherms generally showing the upturns at high elongations that are the signature of good reinforcement.[36,37] Typical results are shown in the left portion of Figure 8.3, where α is the extension.[38] As is generally the case in filled elastomers, there is seen to be considerable irreversibility in the isotherms, which is thought to be due to irrecoverable sliding of the chains over the surfaces of the filler particles upon being strained. The right portion of the figure documents the reinforcement observed in biaxial extension. The maxima and minima exhibited by such results will be a challenge to those seeking a better molecular understanding of filler reinforcement in general.

Some fillers other than silica, for example titania (TiO_2), do give stress-strain isotherms that are reversible, indicating interesting differences in surface chemistry, including increased ability of the chains to slide along the particle surfaces.[39] Such results are illustrated in Figure 8.4.[39] The bonding of PDMS to silica, titania, or silica-titania mixed oxide particles is however strong enough to suppress *swelling* of the polymer, as is illustrated in Figure 8.5.[40] These results involve equilibrium swelling measurements obtained on unfilled and filled PDMS elastomers to estimate the degree of adhesion between elastomer and filler particles.[40–42] The results differ greatly from

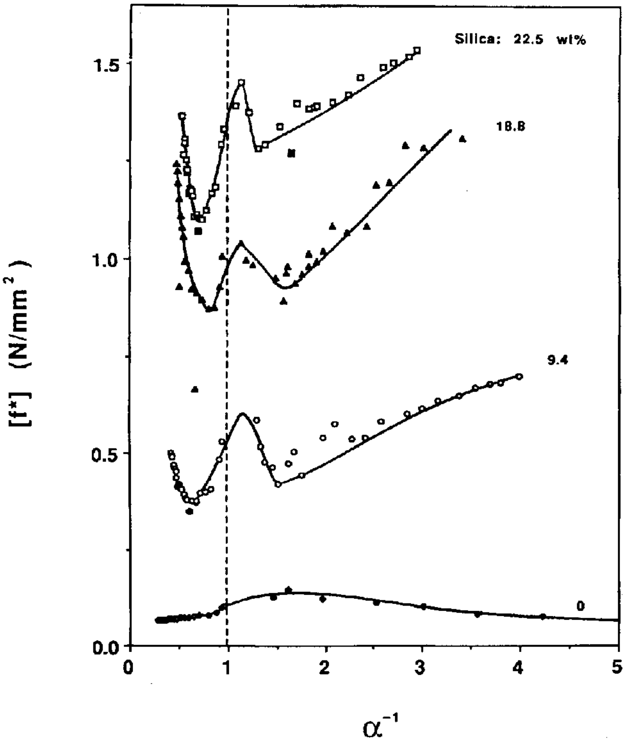

Figure 8.3 Stress–strain isotherms for PDMS-silica in situ reinforced elastomers in elongation (region to the left of the vertical dashed line, with $\alpha^{-1} < 1$), and in biaxial extension (compression) (to the right, with $\alpha^{-1} > 1$).[38] The filled symbols represent the data obtained out of sequence to test for reversibility.

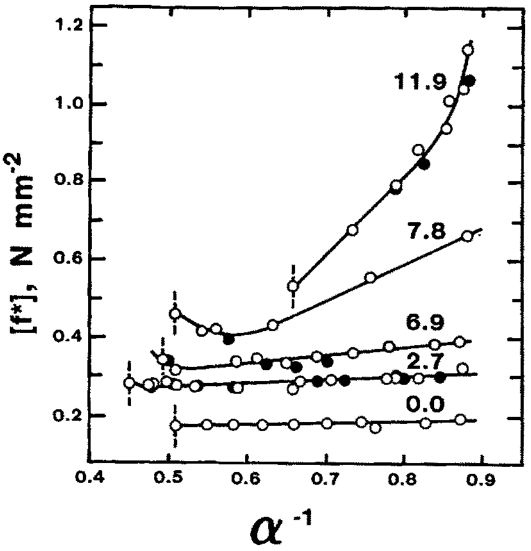

Figure 8.4 Stress–strain isotherms for PDMS networks reinforced with in situ generated titania particles.[39] Each curve is labeled with the wt % of filler introduced, and filled circles locate results used to test for reversibility.

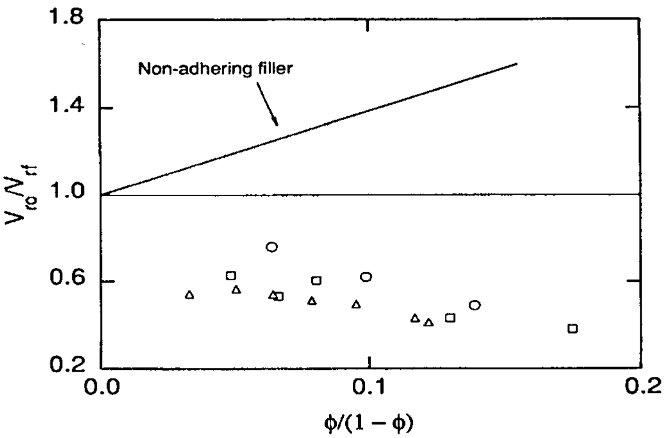

Figure 8.5 Plot of volume fraction ratio V_{ro}/V_{rf} characterizing the swelling of an unfilled PDMS network relative to that of a filled PDMS network, against filler loading expressed as volume ratio of filler to PDMS $\phi/(1-\phi)$ (where ϕ is the volume fraction of filler).[40] Types of filler were silica-titania mixed oxides (□), silica (○), and titania (△).

those to be expected for non-adhering fillers, indicating good bonding between the two phases. Obviously, resistance to separation from the surface in such swelling tests does not contradict the chains having considerable mobility *along* the surfaces of some types of particles, as was just described.

These in situ generated silica fillers also give increased resistance to creep or compression set in cyclic deformations, as is illustrated in Figure 8.6.[43] The in situ filled PDMS samples are seen to show very little compression set. They can also provide increased thermal stability, as demonstrated by the results presented in Figure 8.7.[44]

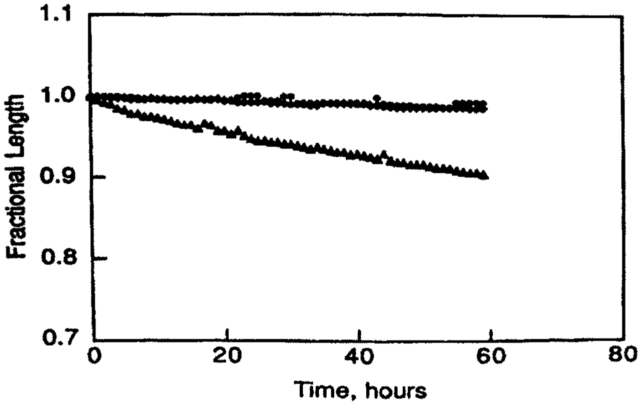

Figure 8.6 Effect of cyclic stress on unfilled PDMS and PDMS elastomers filled with in situ precipitated silica: (▲) unfilled, (●) 12.0 or 19.4 wt % silica.[43]

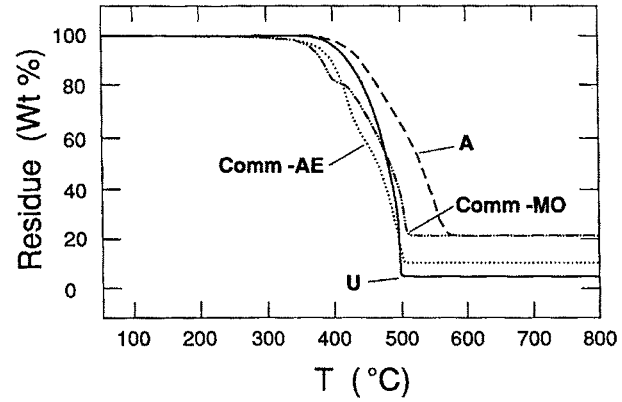

Figure 8.7 Comparison of thermogravometric plots for PDMS networks that were unfilled (U), or contained either in situ precipitated silica (A) or commercial fume silica (COMM-MO and COMM-AE).[44] The heating of the samples was carried out under nitrogen.

The samples in which the SiO_2 was introduced in situ have higher decomposition temperatures. A possible mechanism for this improvement would be increased capability of the in situ produced silica to tie up hydroxyl chain ends that participate in the degradation reaction.

A variety of techniques have been used to further characterize these in situ filled elastomers.[16,18] Density measurements, for example, yield information on the nature of the particles. Specifically, the densities of the ceramic-type particles are significantly less than that of silica itself, and this suggests that the particles presumably contain some unhydrolyzed alkoxy groups or some voids, or both.

The low-temperature properties of some of these peculiarly filled materials have also been studied by the calorimetry techniques mentioned in Chapter 2. Of particular interest is the way in which reinforcing particles can affect the crystallization of a polysiloxane, both in the undeformed state and at high elongations.[45]

As already mentioned, electron microscopy (both transmission and scanning) has been used to characterize the precipitated particles. The information obtained in this way includes (i) the nature of the precipitated phase (particulate or non-particulate), (ii) the average particle size, if particulate, (iii) the distribution of particle sizes, (iv) the degree to which the particles are well defined, and (v) the degree of agglomeration of the particles.[18]

A number of studies using X-ray and neutron scattering[46–49] have also been carried out on filled PDMS elastomers.[16,17] Although the results are generally consistent with those obtained by electron microscopy, there are some intriguing differences. Of particular interest is the observation that some fillers that appear to be particulate in electron microscopy, appear to consist of a continuously interpenetrating phase by scattering measurements. Additional experiments of this type will certainly be forthcoming.

8.2.2 Glassy Particles Deformable Into Ellipsoidal Shapes

It is also possible to obtain reinforcement of a PDMS elastomer by polymerizing a monomer such as styrene to yield hard glassy domains within the elastomer.[50,51] Low concentrations of styrene give low-molecular-weight polymer that acts more like

a plasticizer than a reinforcing filler. At higher styrene concentrations, however, roughly spherical polystyrene (PS) particles are formed, and good reinforcement is obtained. The particles thus generated are relatively easy to extract from the elastomeric matrix. This means that little effective bonding exists between the two phases. It is possible, however, to get excellent bonding onto the filler particles. One way is to include some trifunctional $R'Si(OC_2H_5)_3$ in the hydrolysis, where R′ is an unsaturated group. The R′ groups on the particle surfaces then participate in the polymerization, thereby bonding the elastomer chains to the reinforcing particles. Alternatively, the $R'Si(OC_2H_5)_3$ can be used as one of the end-linking agents, to place unsaturated groups at the cross-links. Their participation in the polymerization would then tie the PS domains to the elastomer's network structure. In any case, the very good reinforcement provided by the PS domains while in the roughly spherical state is shown in Figure 8.8.[50]

The PS domains have the disadvantage of having a relatively low glass-transition temperature (T_g ≈100 °C)[52–54] and in being totally amorphous. Above their values of T_g they would soften and presumably lose their reinforcing ability. For this reason, similar studies have been carried out using poly(diphenylsiloxane) as the reinforcing phase.[55] This polymer is crystalline, and measurements on copolymers containing diphenylsiloxane blocks indicate it has a melting point (and thus a softening temperature) as high as 550 °C![56,57]

It is possible to convert the essentially spherical PS particles just described into ellipsoids.[18,58–62] First, the PS-PDMS composite is raised to a temperature well above the T_g of PS. It is then deformed, and cooled while in the stretched state. The particles are thereby deformed into ellipsoids, and retain this shape when cooled. Uniaxial deformations of the composite give prolate (needle-shaped) ellipsoids, and biaxial deformations give oblate (disc-shaped) ellipsoids.[59,63] Prolate particles can be thought of as a conceptual bridge between the roughly spherical particles used to reinforce elastomers and

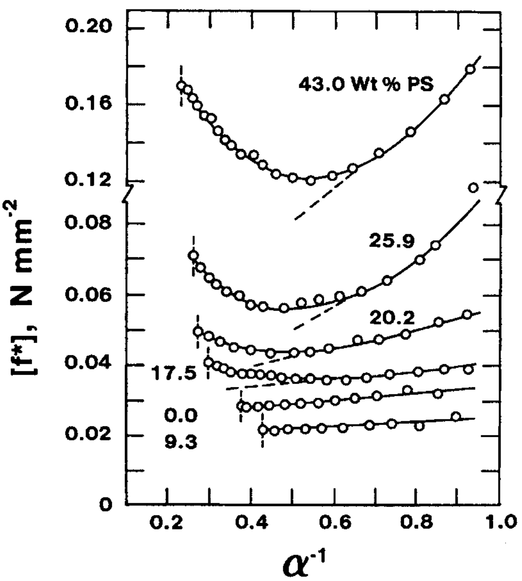

Figure 8.8 Stress–strain isotherms for PDMS-polystyrene (PS) composites.[50] Each curve is labeled with the wt % PS present in the composite, and the dashed lines locate the relatively linear portions of the curves useful for quantitative interpretations.[129]

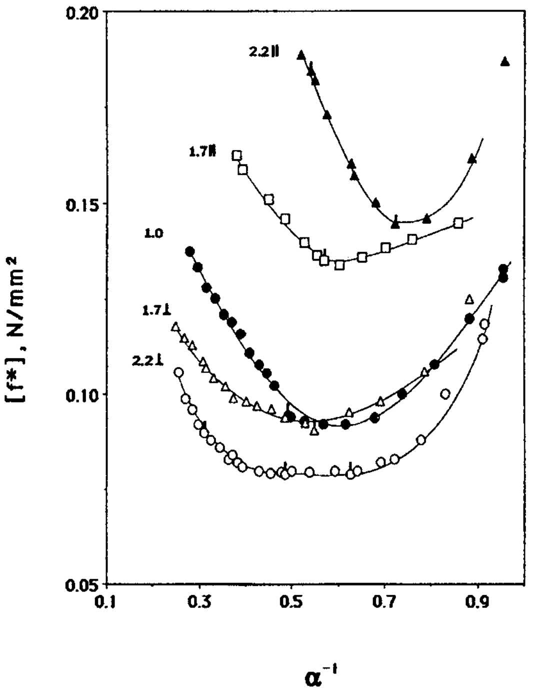

Figure 8.9 Stress–strain isotherms of the PDMS-PS composites described in the preceding figure.[59] Values of the draw ratio and testing directions are indicated on each curve. The symbols with small tabs attached represent data used to test for reversibility.

the long fibers frequently used for reinforcement in thermoplastics and thermosets. Similarly, oblate particles can be considered as analogues of the much studied clay platelets used to reinforce a variety of polymers,[64–67] but with dimensions and compositions that are controllable. Such ellipsoidal particles have been characterized using both scanning and transmission electron microscopy. This gives values for their axial ratios and provides a measure of the extent to which their axes were aligned in the direction of stretching. In these anisotropic materials, elongation moduli in the direction of the stretching were found to be significantly larger than those of the untreated PS-PDMS elastomer, whereas in the perpendicular direction they were significantly lower. This is shown in Figure 8.9.[59] Such differences were to be expected from the anisotropic nature of the systems. In the case of non-spherical particles in general, degrees of orientations are also of considerable importance. One interest here is the anisotropic reinforcements such particles provide, and there have been simulations to better understand the mechanical properties of such composites.[68–70]

8.2.3 Magnetic Particles

Incorporating reinforcing particles that respond to a magnetic field is important with regard to aligning even spherical particles to improve mechanical properties anisotropically.[71–74] Considerable anisotropy in structure and mechanical properties can be obtained, as is demonstrated for PDMS in Figure 8.10.[73] Specifically, the reinforcement is found to be significantly higher in the direction parallel to the magnetic lines of force.

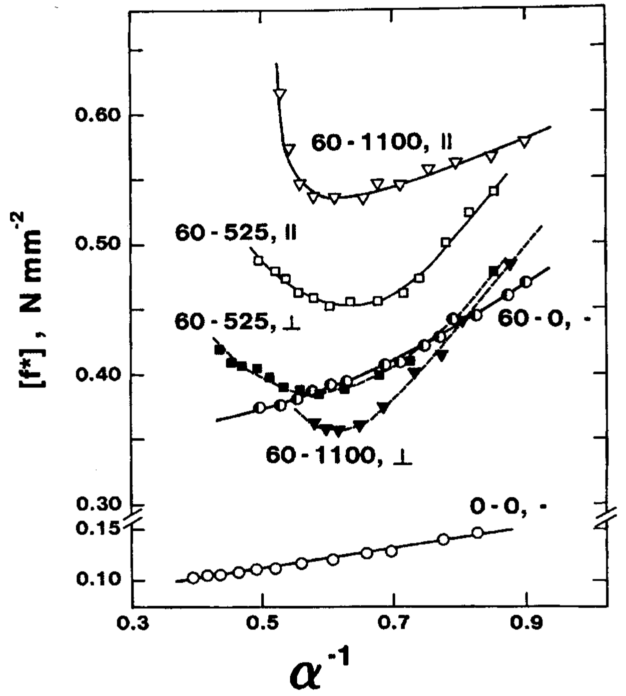

Figure 8.10 Stress–strain isotherms for PDMS composites containing magnetically responsive particles.[73] Each curve is identified by the wt % filler present, the strength of the magnetic field (in Gauss) applied during cross-linking, and the orientation (parallel or perpendicular) of the sample strip relative to the lines of force of the magnetic field.

This technique could be combined with the in situ approach by generating metal or metal oxide magnetic particles in a magnetic field,[75,76] for example by the thermolysis or photolysis of a metal carbonyl. As mentioned earlier, some related work involved the use of in situ techniques to generate electrically conducting fillers such as polyaniline within PDMS.[28]

8.2.4 Layered Fillers

Exfoliating layered particles such as the clays, mica, or graphite is being used to provide very effective reinforcement of polymers at loading levels much smaller than in the case of solid particles such as carbon black and silica.[77–81] Other properties can also be substantially improved, including increased resistance to solvents, and reduced permeability and flammability. A number of such studies specifically address the effects of introducing layered fillers into polysiloxanes.[42,82–88]

8.2.5 Polyhedral Oligomeric Silsesquioxanes (POSS)

These fillers are cage-like silicon-oxygen structures, and have been called the smallest possible silica particles.[89–94] The most common structure has eight silicon atoms, each carrying an organic group. The particles on which none of the groups are functionally reactive can be simply blended into elastomers such as PDMS using the usual mixing

or compounding techniques. In this case, the inert groups are chosen to improve miscibility with the elastomeric host matrix. POSS molecules having one reactive functional group can be attached to a polymer as side chains. Those with two reactive groups can be incorporated into polymer backbones by copolymerization, and those with more than two can be used for forming cross-links, within network structures.

8.2.6 Nanotubes

Carbon nanotubes are also of considerable interest with regard to both reinforcement and possible increases in electrical conductivity.[89,90,92,93,95–104] There is considerable interest in characterizing the flexibility of these nanotube structures, in minimizing their tendencies to aggregate, and in maximizing their miscibilities with inorganic as well as organic polymers.

8.2.7 Porous Fillers

Some fillers such as zeolites are sufficiently porous to accommodate monomers, which can then be polymerized. This threads the chains through the cavities, with unusually intimate interactions between the reinforcing phase and the host elastomeric matrix.[96,105,106] Such an arrangement is illustrated in Figure 8.11. Unusually good reinforcement is generally obtained. Also, because of the constraints imposed by the cavity walls, these confined polymers frequently show no glass-transition temperatures or melting points.[69,107]

PDMS chains have also been threaded through cyclodextrins, to form *pseudo*-rotaxanes.[108]

8.2.8 Fillers with Controlled Interfaces

By choosing the appropriate chemical structures, chains that span filler particles in a PDMS-based composite can be designed so that they are either durable, are breakable irreversibly, or are breakable reversibly.[109–112]

8.2.9 Silicification and Biosilicification

There has been some interest in generating silica-like particles using templates, as is done by Nature in biosilicification processes.[113–118] Various particle shapes have been obtained, and platelet forms would be of particular interest with regard to their abilities to provide reinforcement and decrease permeability.

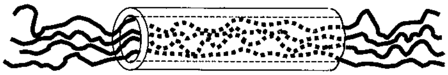

Figure 8.11 Polymer chains being threaded through a porous inorganic material such as a zeolite by polymerizing monomer that had been absorbed into one of the channels or cavities.

8.2.10 Miscellaneous Fillers

There is a variety of miscellaneous fillers that are of interest for reinforcing elastomers such as PDMS. Examples are ground-up silica xerogels,[119] carbon-coated silica,[120] and functionalized silica particles.[121–123]

8.2.11 Simulations on Fillers

Monte Carlo computer simulations have been carried out on a variety of filled elastomers, including PDMS,[124–127] in an attempt to obtain a better molecular interpretation of how such dispersed phases reinforce elastomers. The approach taken enabled estimation of the effect of the excluded volume of the filler particles on the network chains and on the elastic properties of the networks. In the first step, distribution functions for the end-to-end vectors of the chains were obtained by applying Monte Carlo methods to rotational isomeric state representations of the chains.[128] Conformations of chains which overlapped with any filler particle during the simulation were rejected. The resulting perturbed distributions were then used in the three-chain elasticity model[129] to obtain the desired stress–strain isotherms in elongation.

In one application, a filled PDMS network was modeled as a composite of cross-linked polymer chains and spherical filler particles arranged in a regular array on a cubic lattice.[130] The filler particles were found to increase the non-Gaussian behavior of the chains and to increase the moduli, as expected. It is interesting to note that composites with such structural regularity have actually been produced,[131] and some of their mechanical properties have been reported.[132,133] In a subsequent study, the reinforcing particles were randomly distributed within the PDMS matrix.[127] One effect of the filler was to increase the end-to-end separations of the chains. These results on the chain-length distributions are in agreement with some subsequent neutron scattering experiments on silicate-filled PDMS.[134] The corresponding stress–strain isotherms in elongation showed substantial increases in stress and modulus with increase in filler content and elongation that are in at least qualitative agreement with experiment.

In the case of non-spherical filler particles, it has been possible to simulate the anisotropic reinforcement obtained, for various types of particle orientation.[68,70,127,135] Different types and degrees of particle agglomeration can also be investigated.

8.3 Polymer-Modified Ceramics

If the hydrolyses in silane precursor-polymer systems are carried out using relatively large amounts of the silane, then the silica generated can become the continuous phase, with the elastomeric polysiloxane dispersed in it.[12–14,136–143] Again, a variety of ceramic components and polymeric components have been studied. The resultant composite is a polymer-modified glass or ceramic, frequently of very good transparency. Although its thermal stability will be inferior to that of the ceramic component itself, there are many applications for ceramic-type materials where this is not a serious problem.

As might be expected, the properties of these materials depend greatly on the relative amounts of the two phases. Properties of particular interest are modulus, impact resistance, ultimate strength, maximum extensibility, viscoelastic responses, and transparency.

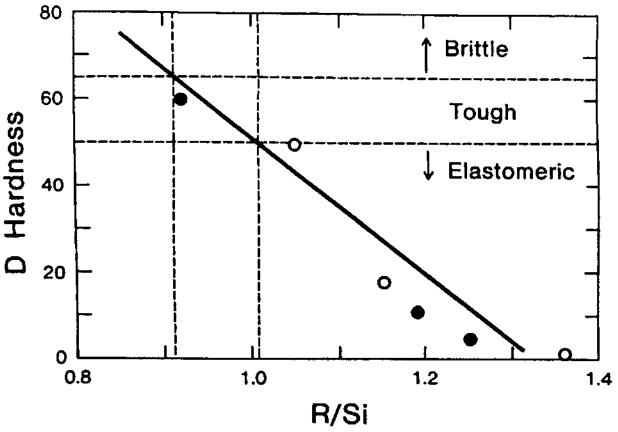

Figure 8.12 The hardness of a silica-PDMS composite as a function of the relative numbers of alkyl groups and silicon atoms.[138] Reproduced by permission of Springer Verlag.

The hardness of such a composite, for example, can be varied by control of the molar ratio of alkyl R groups to Si atoms, as is illustrated for PDMS in Figure 8.12.[138] Low values of R/Si yield a brittle ceramic, and high values give a relatively hard elastomer. The most interesting range, R/Si ≅ 1, can yield a relatively tough ceramic of increased impact resistance.

Some improvements in impact strength in such composites are illustrated in Figure 8.13.[144] Specifically, impact strengths of some PDMS-SiO_2 samples were determined by the Charpy pendulum test and by the falling-weight test.[144] The samples investigated were PDMS-modified SiO_2 and SiO_2/TiO_2 glasses with PDMS contents ranging from 0 to 65 wt %. As expected, only samples with relatively high ceramic contents were sufficiently brittle to be studied in this manner. As can be seen from the figure, the larger the amount of PDMS used, the higher the impact strength.

For PDMS-modified SiO_2 glasses, structural analysis shows that this hybrid material has some degree of localized phase separation of the PDMS component, even though OH-terminated PDMS can be successfully incorporated into the SiO_2 network by chemical bonding. The PDMS component can behave as an elastomeric phase because the glass-transition temperature of PDMS is far below room temperature.[52–54]

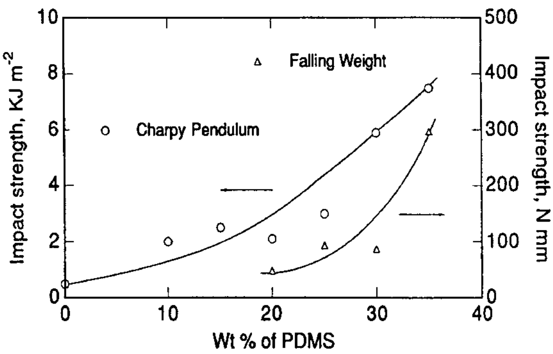

Figure 8.13 Dependence of two estimates on the impact strength on the amount of PDMS in PDMS-modified SiO_2 glasses.[144] The impact strengths were obtained from: (○) the Charpy pendulum impact test; (△) the falling-weight impact test.

When the material is subjected to an impact test, the PDMS component can absorb a great deal of energy by motions of the PDMS chains, and can ameliorate the growth of cracks and fracture. Therefore, considerable toughening of the glass can be achieved by increasing the amount of PDMS introduced. The impact resistance was also observed to increase in with increase in PDMS molecular weight, possibly due to increase in the phase separation which leads to the energy-absorbing domains.[144]

Also relevant here are some microscopy results. Microscopy of fracture surfaces of brittle samples typically shows smooth fracture surfaces,[145] with little evidence of effective resistance to either initiation or propagation of cracks. This was observed in the case of the composite silica samples having relatively low PDMS contents. In contrast, samples with high PDMS contents had fracture surfaces showing some degree of "whitening" or shearing.[144] This suggests a ductile, energy-absorbing response to the impacts, with increased resistance to crack propagation.

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9

Preceramic Inorganic Polymers

9.1 Overview of Ceramic Aspects

One of the most important interfaces in materials science is the one between polymers and ceramics.[1–11] Ceramics can be viewed as highly cross-linked polymer systems, with the three-dimensional network providing strength, rigidity, and resistance to high temperatures. Although not generally recognized as such, a few ceramics exist that are totally organic (i.e., carbon-based). Melamine-formaldehyde resins, phenol-formaldehyde materials, and carbon fibers are well-known examples.[12] However, totally inorganic ceramics are more widely known, many of which are based on the elements silicon, aluminum, or boron combined with oxygen, carbon, or nitrogen.[1–11]

Among the inorganic ceramics, two different classes can be recognized—oxide ceramics and non-oxide materials. The oxide ceramics frequently include silicate structures, and these are relatively low melting materials. The non-oxide ceramics, such as silicon carbide, silicon nitride, aluminum nitride, and boron nitride are some of the highest melting substances known. Non-oxide ceramics are often so high melting that they are difficult to shape and fabricate by the melt- or powder-fusion techniques that are common for oxide materials.

One major use for inorganic-organic polymers and oligomers is as sacrificial intermediates for pyrolytic conversion to ceramics. The logic is as follows. Linear, branched, or cyclolinear polymers or oligomers can be fabricated easily by solution- or melt-fabrication techniques. If a polymeric material that has been shaped and fabricated in this way is then cross-linked and pyrolyzed in an inert atmosphere to drive off the organic components (typically, the side groups), the resultant residue may be a totally inorganic ceramic in the shape of the original fabricated article. Thus, ceramic fibers, films, coatings, and shaped objects may by accessible without recourse to the ultra-high temperatures needed for melting of the ceramic material itself.

Note, however, that although the final *shape* of the object may be retained during pyrolysis, the *size* will be diminished due to the loss of volatile material. If the pyrolysis takes place too quickly, this contraction process may cause cracking of the material and loss of strength. Moreover, too rapid a rate of heating before or during the initial cross-linking step may cause the polymer intermediate to melt and lose its shape, or the polymer may depolymerize and the products volatilize. Thus, the "temperature program" or the sequence and rate at which the temperature is raised can have a profound influence on the final properties.

Figures 9.1–9.3 illustrate these interconnected relationships.[13] Figure 9.1 defines some of the terms used in this chapter. Small molecules are species with molecular weights below about 1,000. They are volatile at temperatures below say 200–400 °C. Clusters are oligomers derived from covalently linked small molecules. They have a lower volatility than small molecules and, if large enough, can be shaped by melting or by solvent evaporation methods. Linear polymers can be simple chain structures or may consist of rings linked together. In either case they are usually non-volatile and easily fabricated. Cross-linked systems can be produced from polymers or from clusters. The final ceramic may be amorphous or crystalline.

Figure 9.2 shows how heating of the initial preceramic polymer or oligomer must be carefully correlated with cross-linking. Unless cross-linking occurs first the polymer will decompose to volatile small molecules that will be lost from the system. It is conceivable that in a closed system some of these small molecules could be captured and linked into the network, but this is uncommon. Ceramics are generally accessible only through the cross-linked network.

Figure 9.3 further illustrates these principles and adds another aspect. This is the possibility that the pyrolysis process may involve loss of the polymer backbone and formation of the ceramic from the side groups. Thus, an organic polymer with inorganic side groups might be utilized in this way. However, this is an inefficient use of the carrier polymer and there are relatively few examples of this approach.

In the following sections some examples are given of the ways in which these principles have been utilized. The first example is the use of these techniques for the low temperature preparation of oxide ceramics such as silica. This process can also be used to produce alumina, titanium oxide, or other metal oxides. The second example describes the conversion of organic polymers to carbon fiber, a process that was probably the inspiration for the later development of routes to a range of non-oxide ceramics. Following this are brief reviews of processes that lead to the formation of silicon carbide, silicon nitride, boron nitride, and aluminum nitride, plus an introduction to the synthesis of other ceramics such as phosphorus nitride, nitrogen-phosphorus-boron materials, and an example of a transition metal-containing ceramic material.

9.2 The Sol-Gel Process to Oxide Ceramics

Starting in the 1950s a process was developed that leads from small-molecule silicon alkoxides such as tetraethoxysilane (tetraethyl orthosilicate), to organosiloxane oligomers and low polymers, and eventually to silica via a "low temperature" synthesis route.[14–24] A simplified outline of the basic chemistry is shown in reactions (1)–(4), where R is an ethyl or higher alkyl unit. Any or all of the Si-OR bonds can be

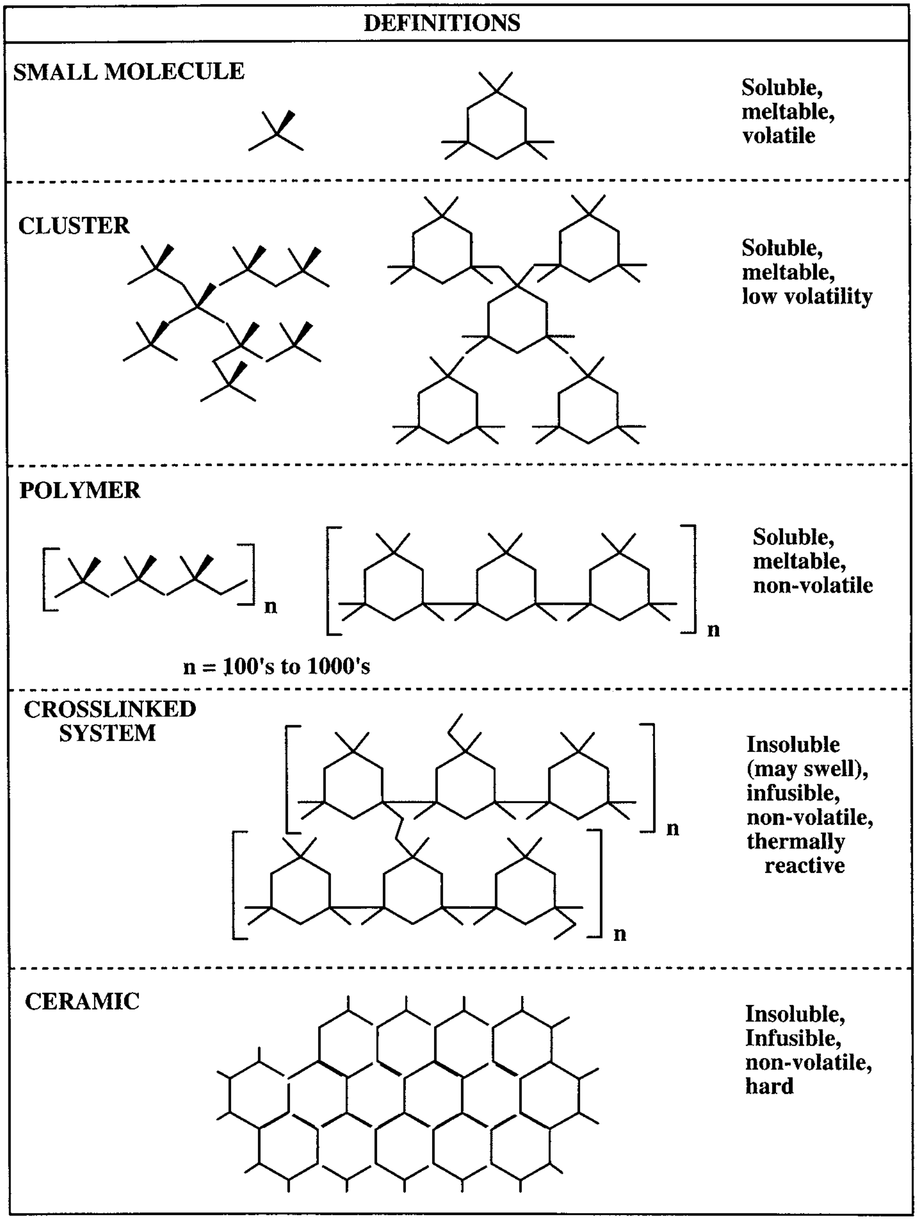


Figure 9.1 Definitions of the various species used as starting materials and condensation products during pyrolytic conversion to ceramics.

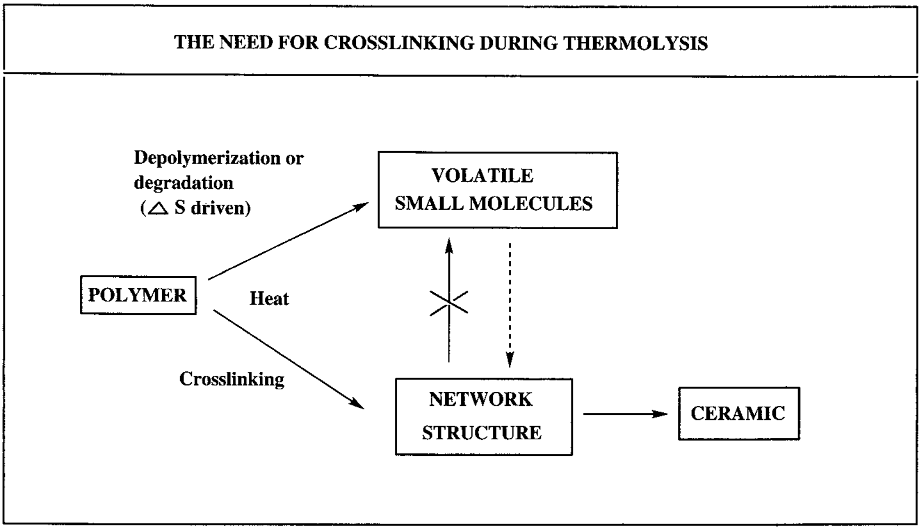


Figure 9.2 Illustrating the crucial need for cross-linking the preceramic polymer at an early stage in the pyrolysis to prevent loss of material in the form of volatile decomposition or depolymerization products.

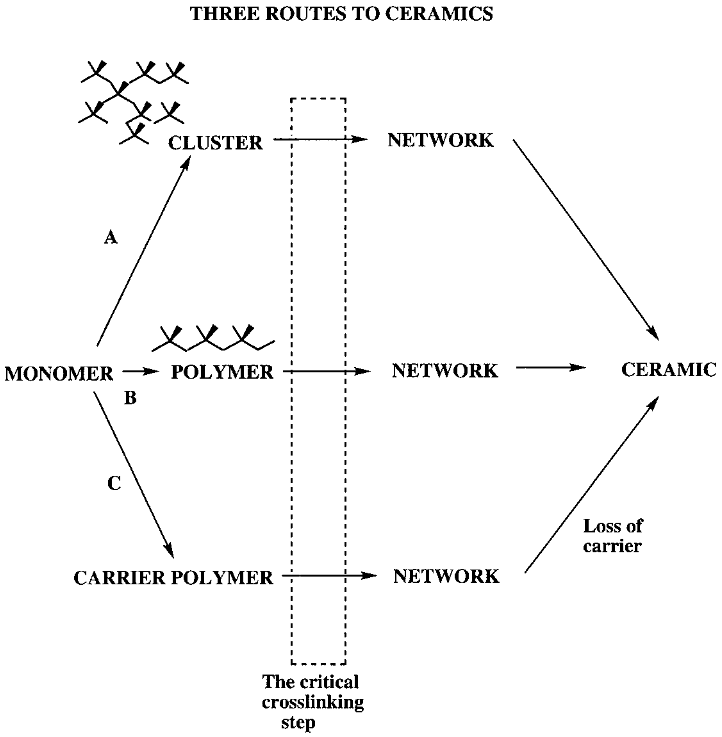
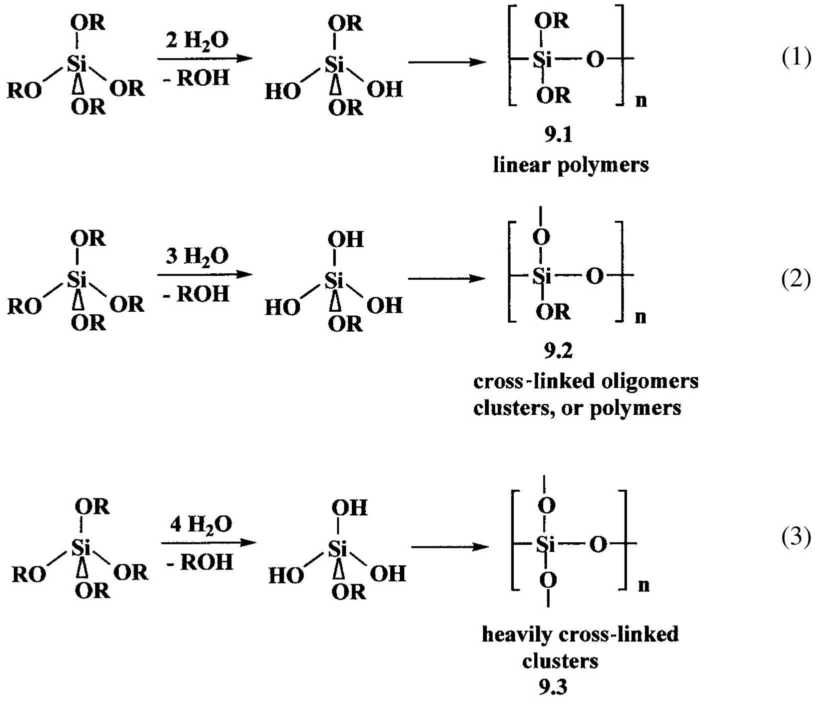


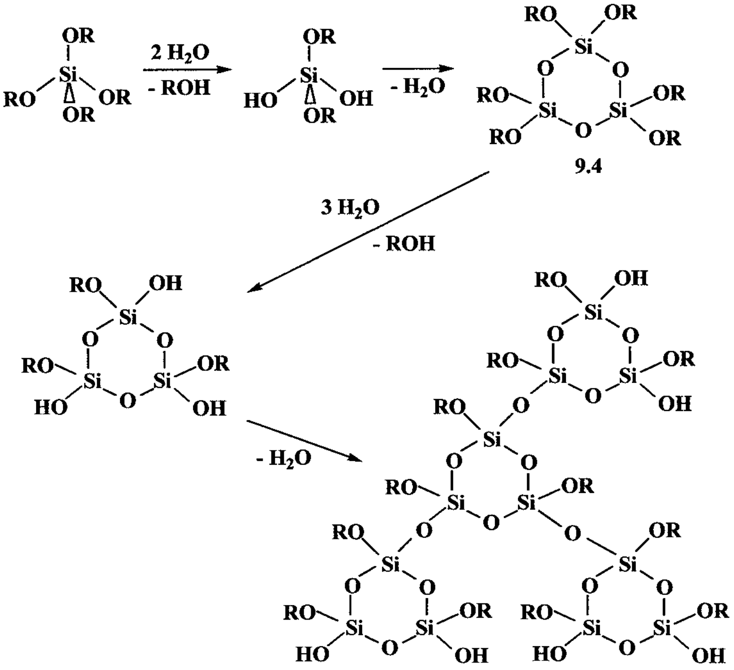
Figure 9.3 Three routes to ceramics all of which proceed through a vital crosslinking process to give a network early in the pyrolysis program. In pathway C the carrier polymer is decomposed during pyrolysis and the side groups are incorporated into the final ceramic.

hydrolyzed to Si-OH functional groups, and these are able to condense to form Si-O-Si linkages. The linear polymers (**9.1**) formed in reaction (1) can undergo further alkoxide hydrolysis to give the cross-linked species, **9.2**, also formed in reaction (2), and these cross-linked polymers may further cross-link to give an ultrastructure similar the one formed in reaction (3).



Moreover, step (1) could generate six-, eight- or higher membered rings instead of chains, and these rings may couple to yield clusters of rings (reaction sequence (4)). Although cyclic trimeric siloxane rings are shown for simplicity in reaction (4), the most probable products are cyclic tetramers and higher cyclics. Reaction (2) could also generate cage structures and these too could become linked to form clusters. Subsequently, the alkoxy groups on the outer boundaries of the ring or cage clusters can hydrolyze and couple to other clusters to yield clusters of clusters, and so on. Ring clusters may, in principle, react with chain clusters or linear polymers to increase the structural complexity. Eventually a catastrophic gelation of the system will occur, and what was originally a solution or a colloid will become a solvent-swollen solid in the shape of the original reaction vessel or mold. Subsequent heating to drive off water and alcohol will complete the condensation process and leave an amorphous form of silica.

The complexity of this reaction mechanism is legendary. The reaction pathways and types of products change with variations in pH, the nature of the alkoxy group OR, the rate at which water and alcohol are removed during heating, the type of solvent, the



(4)

presence of other metal alkoxides, or the existence of functional organic molecules that can enter into the condensation process. The addition of transition metal alkoxides provides a means for the introduction of color into the final ceramic, an option that is useful for the fabrication of optical filters, colored coatings, or ceramic art objects.

Variations in pH, concentration, and temperature have a profound effect on the condensation pathway. Acidic media, high concentrations of reagents, and lower temperatures favor the formation of chains or loosely cross-linked chains. Basic media, dilute solutions, and higher temperatures favor the formation of rings, cages, and cluster networks (Figure 9.4).

Processing conditions also determine the types of products that are formed, as shown in Figure 9.5. For example, fibers can be pulled from a system that contains colloidal clusters that have not yet gelled. Evaporation of a colloidal suspension or a solution may give a "xerogel" coating. Once the system has gelled, extraction of the remaining small molecules using a volatile solvent will leave an "aerogel" which has volume and shape, but is mostly unfilled space. Such materials have been used in flotation devices, lightweight structural materials, or filters. Evaporation of the solvent from a gel allows contraction of the system to a xerogel, and subsequent heating above the melting point gives a dense glass. This is a way to produce lens preforms. Composite materials called "ceramers" are accessible if a water- or alcohol-soluble organic polymer is included in the original reaction mixture. The organic polymer raises the impact resistance of the final ceramic.

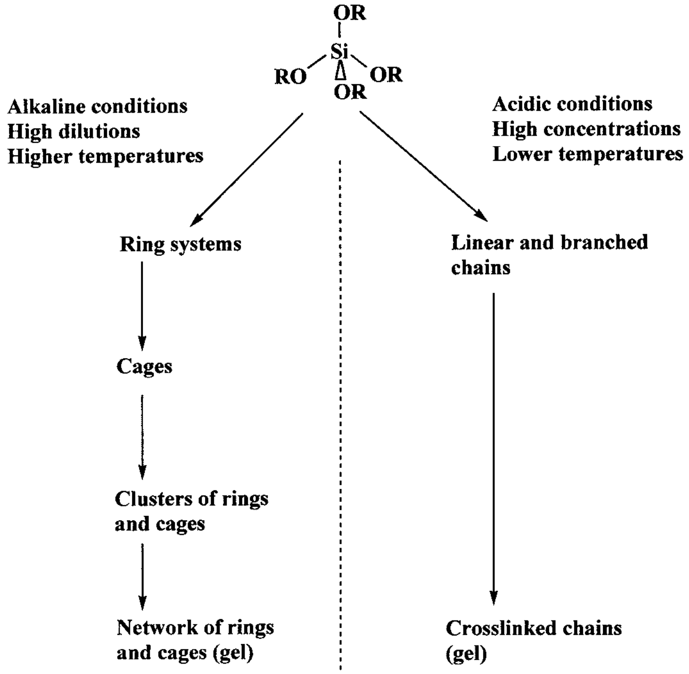


Figure 9.4 Reaction conditions exert a strong influence on the course of a sol-gel polymerization reaction. Basic pH, higher temperatures, and greater dilutions favor the formation of rings and ring clusters, as shown in the pathway on the left. Acidic pH, lower temperatures, and higher concentrations favor the formation of chains and dendritic structures.

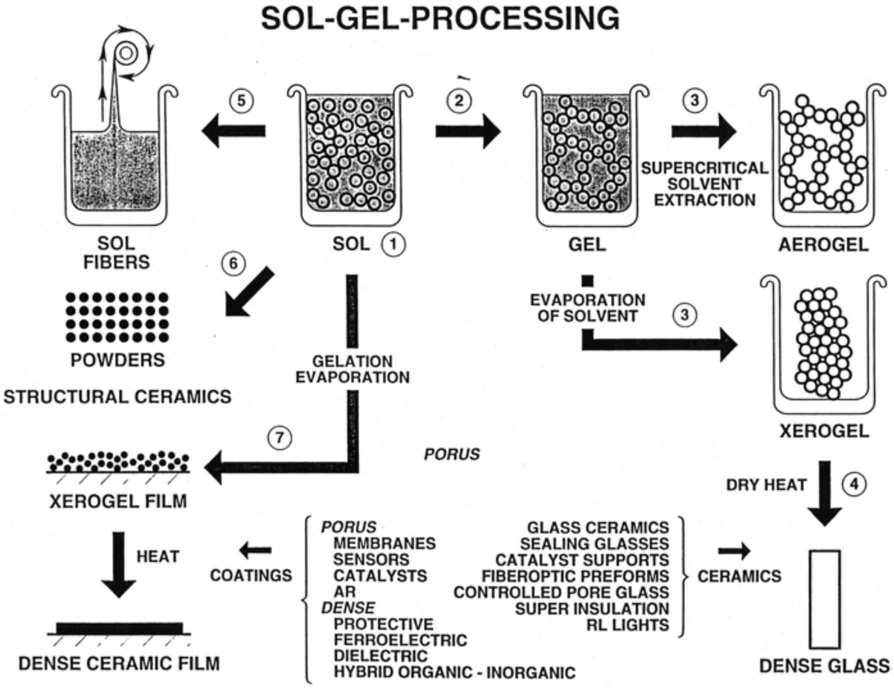


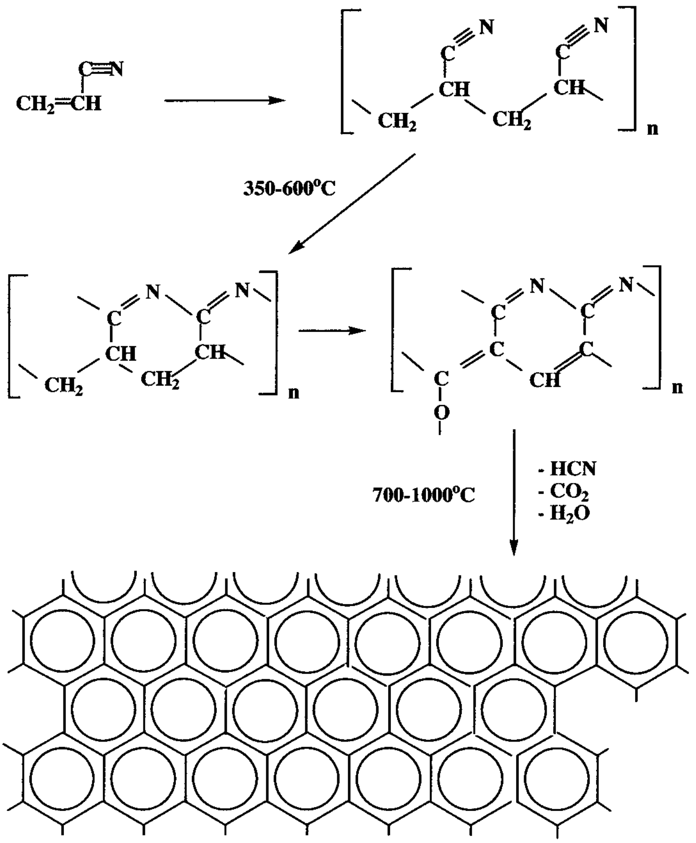
Figure 9.5 Various procedures for processing a sol-gel reaction mixture lead to different types of materials. Reproduced by permission of C.J. Brinker.

9.3 Carbon Fiber

Carbon fiber is a graphitic material with high strength, resistance to thermal decomposition, and the ability to conduct an electric current.[25] A carbon fiber cloth can be heated with a propane torch without burning. It glows red but resists breakdown for a long time. Carbon fiber is produced by the pyrolytic conversion of an organic polymer, such as poly(acrylonitrile) or regenerated cellulose (Rayon), to carbon under non-oxidative conditions. The organic polymer is first spun into fibers. The fibers may then be woven into a cloth. Pyrolysis drives off small molecules to leave a black, graphitic material in the shape of the original fiber or cloth. Carbon fibers and carbon cloth are widely used in composites in aircraft and space vehicles because of their strength, heat resistance, inertness, and lightweight character.

Carbon fiber is produced from several different organic polymers, but polyacrylonitrile has many advantages as a starting material. It is easily spun into fibers, and the chemistry of its pyrolysis reactions favors "aromatization" as a pathway to graphite-like structures. The process is outlined in reaction sequence (5).

Pyrolysis can be considered as a three-step process. The first step (stabilization) takes place when poly(acrylonitrile) fibers are heated at 200–300 °C in air. This initiates oxidation and the formation of cross-links. The second phase (known as carbonization)



(5)

involves heating the cross-linked material in high purity nitrogen at 1,200–200 °C. Cyclization of the pendent nitrile groups occurs during this stage to form heterocyclic rings in the structure. The final step (graphitization) takes place during a brief exposure to temperatures above 2,500 °C in nitrogen. All or most of the nitrogen atoms in the structure are finally lost at this point to give what is essentially graphite-like sheets within the fibers. Throughout the pyrolysis sequence molecules such as HCN, H_2O, CO_2, and NH_3 are evolved.

An alternative starting material for carbon fiber production is pitch—a complex mixture of fused polyaromatic hydrocarbon clusters that can also be melt-spun into fibers.

The pyrolytic formation of carbon fiber provides an introduction to the conditions and temperature programming that is required for the formation of ceramics that contain silicon, boron, aluminum, and other elements.

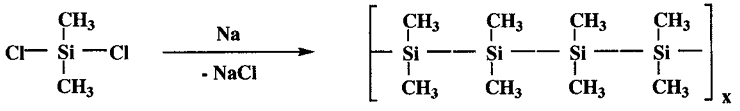
9.4 Silicon Carbide (SiC)

Silicon carbide is a tough, wear-resistant material with a hardness close to that of diamond. It has a very high thermal stability, with decomposition temperatures of 2,985 °C (cubic form) and 2,824 °C (α-form). Moreover, it is highly stable to most aqueous acids, resists bulk oxidation at high temperatures, has a high thermal conductivity and a low coefficient of thermal expansion. It is also an intrinsic semiconductor. Such a material clearly has many uses that range from abrasives (carborundum) and hard coatings for machine tools to fibers and whiskers for use as reinforcing agents in composite materials. The semiconductor properties underlie applications in light emitting diodes and heating elements. Future uses in jet engines, high-temperature heat exchangers, and brakes are under development.

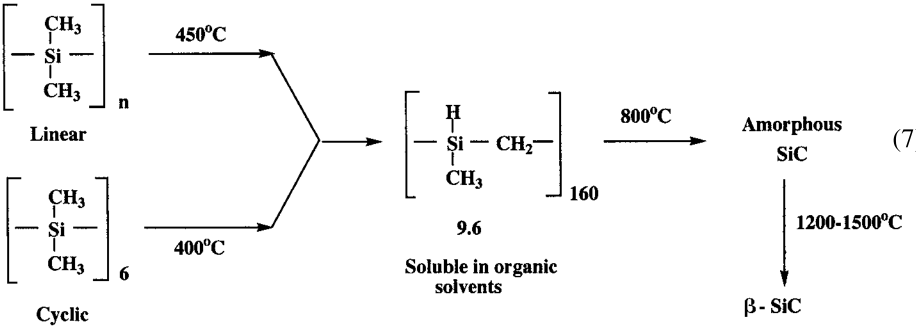
The conventional industrial method for the synthesis of α-silicon carbide is to heat silica (sand) with coke in an electric furnace at 2,000–2,500 °C. However, because of the high melting point of the product, it is difficult to fabricate by sintering or melt techniques. Thus, the discovery of a lower temperature fabrication and synthesis route to silicon carbide by Yajima and coworkers in 1975[26,27] proved to be an important technological breakthrough. This is a preceramic polymer pyrolysis route that has been developed commercially for the production of ceramic fibers.

An outline of the process is as follows. As discussed in Chapter 5, diorganodichlorosilanes react with sodium or sodium-potassium alloy in an organic solvent to yield a mixture of cyclic and linear oligosilanes. If the starting material is Me_2SiCl_2, the product mixture has the composition $(Me_2Si)_x$. This mixture is isolated and heated at 350–450 °C in autoclave to yield a so-called "carbosilane" intermediate (**9.6**). The lower pyrolysis temperature requires the presence of catalysts such as titanium alkoxides or a borosiloxane. The chemistry is summarized in reactions (6) and (7). Although the carbosilane was originally believed to have the simple structure shown as **9.6**, it is now known to be a much more complex species that contains both rings and chain segments, as shown in structure **9.7**.

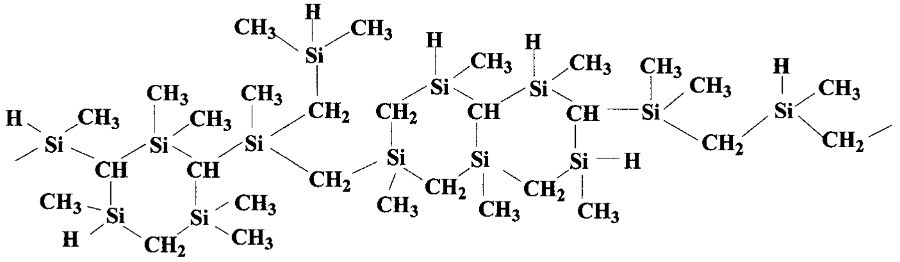
The carbosilane is a white, soluble, and meltable material that can be melt-spun into fibers at 190 °C. Exposure of the fibers to air at the same temperature generates a surface coating of silica which stabilizes the structure throughout the cross-linking step prior to pyrolysis. Subsequent heating at 1,200–1,500 °C in a nitrogen atmosphere drives off



(6)



(7)

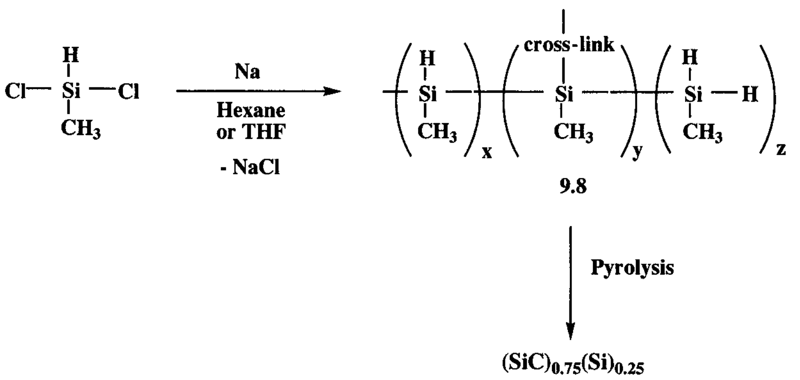


9.7

methane and hydrogen to leave a ceramic fiber (reaction (7)). The overall composition of the fiber is SiC : C : SiO_2 = 1 : 0.78 : 0.22. Thus, the ceramic has an excess of carbon, which is detrimental to the properties. The SiO_2 is mainly in the form of a coating that protects the bulk material in the fiber against oxidation in air at temperatures up to 1,000 °C.

A considerable amount of subsequent research and process development has been carried out to produce silicon carbide with a reduced level of excess carbon via processes that allow more facile cross-linking.[28–32] Several hundred papers and patents on this topic exist in the literature, and only a few examples will be mentioned here. One process development involves the slurry spinning of fibers in place of melt spinning.[33] In this process, silicon carbide powder, made by a conventional industrial process, is dispersed in a solution of carbosilanes in toluene. The syrupy paste is spun into fibers and then pyrolyzed to silicon carbide. These fibers are reported to be stable at 1,500 °C for 120 hours.

An example of the enhanced cross-linking approach involves the pyrolysis of cyclic and linear oligosilane precursors that bear vinyl or acetylenic side groups.[34] These are



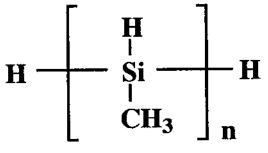
9.8

(8)

capable of yielding formable materials under relatively mild conditions. However, the presence of more than a 1:1 ratio of carbon to silicon in the starting materials leads to excess carbon in the final ceramic product.

Several investigators have used the following strategies to reduce the amount of carbon in the preceramic materials. Seyferth and coworkers developed a process based on $MeSiHCl_2$ as a starting material rather than Me_2SiCl_2.[34,35] Thus, as shown in reaction (8), formation of the cross-linked polysilane intermediate, **9.8**, was followed by pyrolysis to give a *silicon-rich* ceramic. Modifications to this process by the use of organolithium reagents reduced the silicon content in the final ceramic to less than a 0.1:1 ratio of Si to SiC.

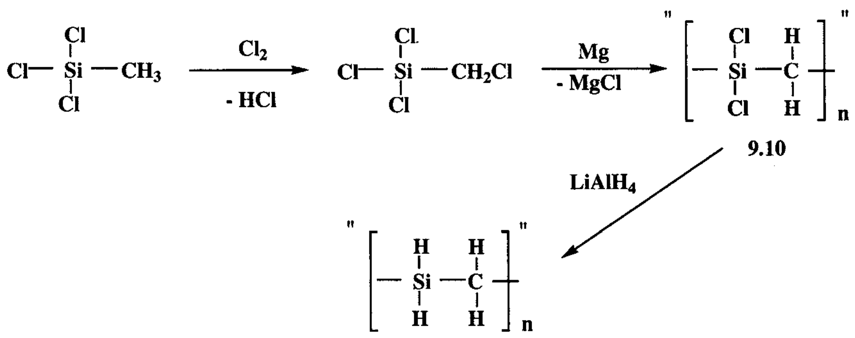
Alternative routes to silicon carbide, based on $MeSiH_3$ as a starting material, have also been developed. For example, when $MeSiH_3$ is heated in the absence of a catalyst, the preceramic intermediate corresponds closely to the one described as **9.8**. However, in the presence of a catalyst[36,37] such as $(\eta^5\text{-}C_5H_5)_2ZrR_2$ (R = H or Me), the product is believed to be the simpler silane structure shown as **9.9**. Both products give silicon-rich silicon carbide following pyrolysis.



9.9

Interrante and coworkers[38] developed a multi-stage process leading to silicon carbide that starts from the readily available $MeSiCl_3$. The reaction sequence is summarized in reaction (9).

Actually, species **9.10** and **9.11** are more complex than the structures shown. They are, in fact, *hyperbranched polysilanes* of the types shown in **9.12**, which are soluble in hydrocarbons and are sufficiently stable to moisture that they can be handled in air.



(9)

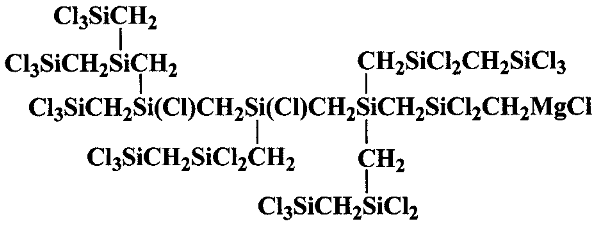
9.11

HPCS

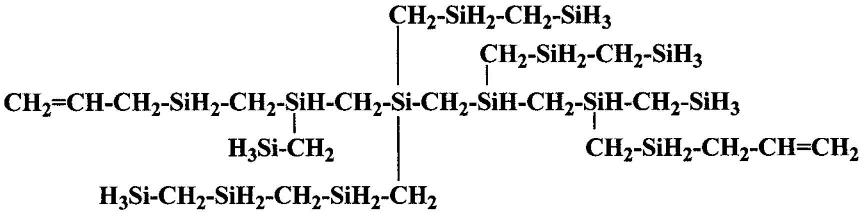
Hyperbranched carbosilane

Although the direct reduction of **9.12** is a viable route to the polysilane, other alternative strategies exist. For example, the treatment of **9.12** with an allyl or vinyl Grignard reagent before reduction gives carbosilane intermediates with allyl or vinyl groups linked to silicon. A structure is shown as **9.13**. The unsaturated groups facilitate cross-linking prior to pyrolysis at 1,000 °C or 1,600 °C.

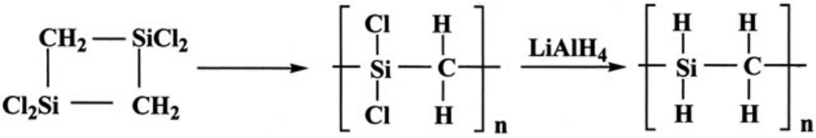
The pyrolysis products from **9.13** can give essentially pure silicon carbide in 89% yield. Intermediates that contain from 5 to 25% allyl functionalized units give ceramics with progressively larger amounts of carbon beyond the 1:1 Si:C ratio. This process has been developed into a manufacturing sequence for the production of reinforced composites for aircraft brakes and high temperature coatings.



9.12



9.13



(10)

9.14

Finally, an alternative route to poly(silylenemethylene) (linear carbosilanes) is via the ring-opening polymerization of a carbosilane cyclic dimer (**9.14**),[39] as shown in reaction (10), or of a cyclocarbosilane with alkoxy groups in place of chlorine. The high-molecular-weight linear polymers (Mn ~ 30,000) formed in this way give 90% yields of stoichiometric silicon carbide when pyrolyzed at 1,000 °C. Cross-linking is achieved by loss of hydrogen as the temperature is raised.

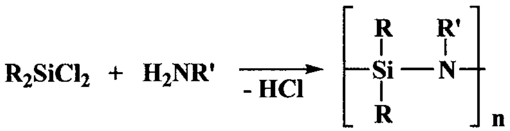
Interrante and coworkers[40] have also produced silicon carbide nanotubes by the deposition of cyclic carbosilanes inside alumina nanotubes, followed by pyrolysis and removal of the alumina in hydrofluoric acid.

9.5 Silicon Nitride (Si_3N_4)

Silicon nitride is prized for its hardness (9 out of 10 on the Mohr scale), its wear resistance, and its mechanical strength at elevated temperatures. It melts and dissociates into the elements at 1,900 °C, and has a maximum use temperature near 1,800 °C in the absence of oxygen and near 1,500 °C under oxidizing conditions.[41] It also has a relatively low density (3.185 g/cm^3). Unlike silicon carbide, silicon nitride is an electrical insulator. The bulk material has a relatively good stability to aggressive chemicals. This combination of properties underlies its uses in internal combustion engines and jet engines.

The traditional synthesis route involves the direct reaction of silicon with nitrogen at temperatures above 1,300 °C, or by heating silica with carbon (coke) in a stream of nitrogen and hydrogen at 1,500 °C.[41] However, as in the case of silicon carbide, the high processing and fabrication temperatures focused attention on the need for alternative access routes based on preceramic polymers.

Some of the starting materials for preceramic synthesis processes are compounds known as polysilazanes. These are oligomers or polymers related to poly(organosiloxanes) (Chapter 4), but with the skeletal oxygen atoms replaced by nitrogen. They are synthesized by the reaction or diorganodichlorosilanes with ammonia or primary amines as shown in reaction (11). These species were investigated in the 1960s[42,43] as possible counterparts to silicones, but their hydrolytic instability proved to be a decisive weakness for normal applications.



(11)

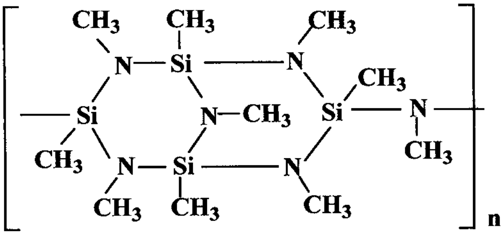
In 1974 Verbeek and Winter[44,45] described a related process in which methyl-*trichloro*silane reacts with methylamine or ammonia to yield a complex oligomer with a structure approximating to **9.15**. This species could be melt-spun to form preceramic fibers which, when cross-linked, were pyrolyzed to amorphous silico-carbo-nitride fibers. The sequence of steps is shown in reaction (12).

The carbon content of the ceramic causes instability at temperatures above 1,400 °C because of a rearrangement to silicon carbide and nitrogen. Hence, as in the case of silicon carbide, strategies for lowering or eliminating the carbon content of the final ceramic have received considerable attention.

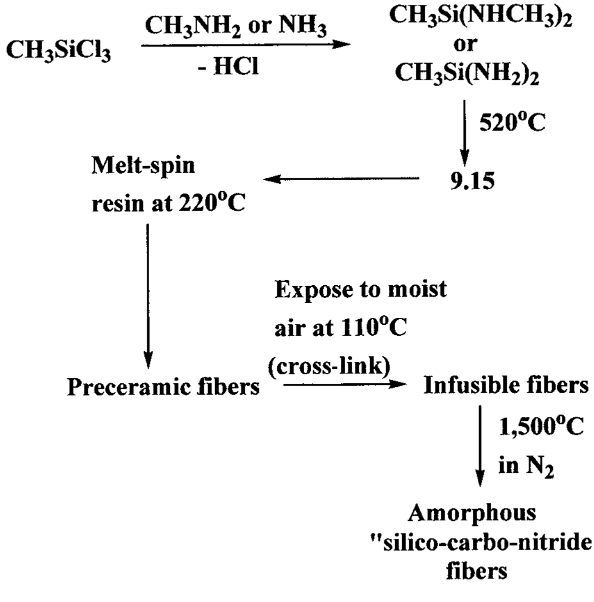
One approach by Nishi[46] starts from a pyridine complex of dichlorosilane which is treated with ammonia, as shown in reaction (13). This process yields essentially pure Si_3N_4, but suffers from the difficulty of handling H_2SiCl_2.

Seyferth and coworkers[9,10,47–50] devised an alternative synthesis based on the use of methyl dichlorosilane. This is shown in reaction (14).

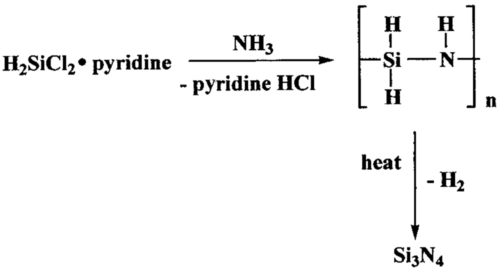
Species **9.16** is believed to have the complex structure depicted in **9.17**, which is formed by the coupling of eight-membered rings to give a cyclo-linear polymer. The excess carbon can be removed from the silico-carbo-nitride by heating with ammonia



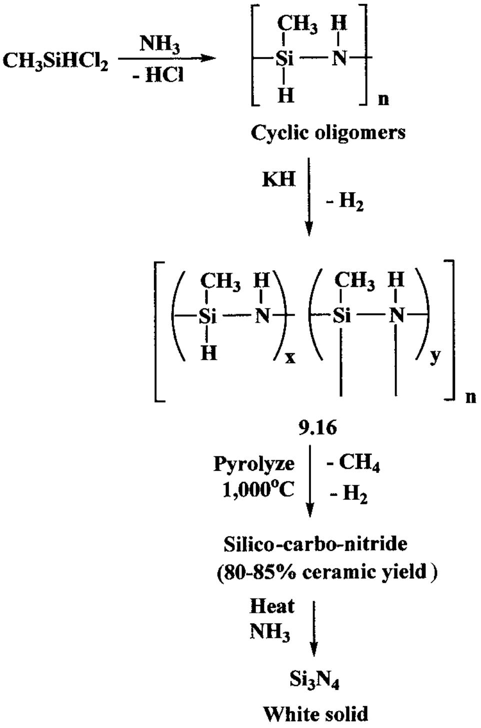
9.15



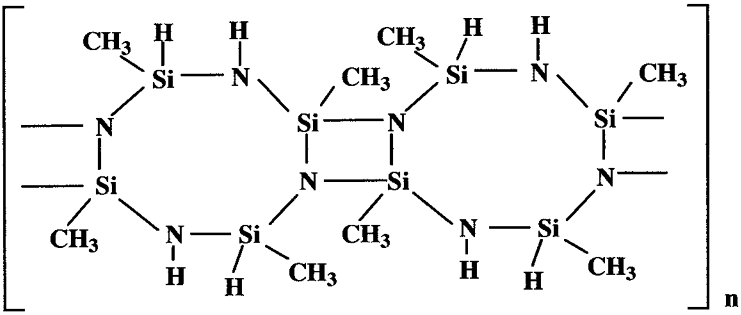
(12)


H2SiCl2• pyridine
NH3
- pyridine HCl
heat
- H2
Si3N4

(13)


CH3SiHCl2
NH3
- HCl
Cyclic oligomers
KH
- H2
9.16
Pyrolyze
1,000°C
- CH4
- H2
Silico-carbo-nitride
(80-85% ceramic yield)
Heat
NH3
Si3N4
White solid

(14)



9.17

n = ~10

at ~1,000 °C.[50,51] Other precursors to Si-C-N and Si_3N_4 are cyclo-tri- and -tetrasilazane rings that bear vinyl side groups to facilitate cross-linking.[52,53]

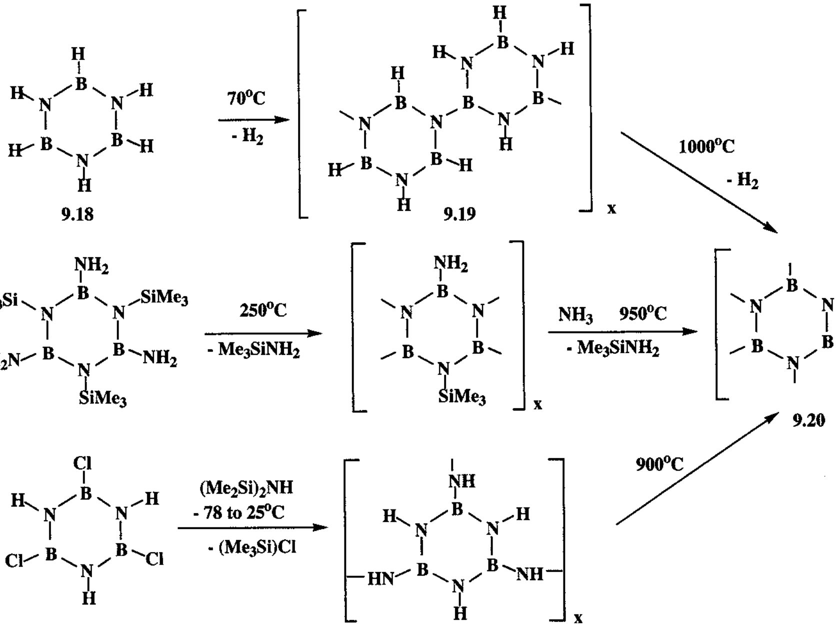
9.6 Boron Nitride (BN)

Boron nitride is a ceramic with outstanding properties. It is thermally stable at temperatures up to 2,730 °C, is a good electrical insulator, and has a high thermal conductivity coupled with excellent thermal-shock resistance. It is also chemically inert.

The traditional method for the preparation of boron nitride is by the fusion of urea with boric acid in an atmosphere of ammonia at 750 °C.[54] The product from these reactions is hexagonal boron nitride with a layer structure like that of graphite. Unlike graphite, it is colorless and is not an electronic conductor. Conversion of the hexagonal form to a cubic modification requires heating at 1,800 °C at 85,000 atmospheres pressure.

Alternative routes to boron nitride have been examined that do not require those challenging reaction conditions. These fall into three categories, which are: (1) the pyrolysis of borazines; (2) pyrolysis of organic or inorganic polymers that bear borazine groups as side units; and (3) pyrolysis of polyhedral borane derivatives.

One of the most logical starting materials for the preparation of boron nitride is borazine (**9.18**) or one of its organic derivatives. Borazine is a colorless liquid prepared by the reaction of boron trichloride with ammonia or ammonium chloride, followed by reduction of the product $(ClB\text{-}NH)_3$ with sodium borohydride. Pyrolysis of borazine, accompanied by loss of hydrogen, gives condensed and ring-linked species analogous to naphthalene or biphenyl (**9.19**).[55–60] Continuation of the process should give hexagonal boron nitride (**9.20**) (reaction (15)).



(15)

(16)

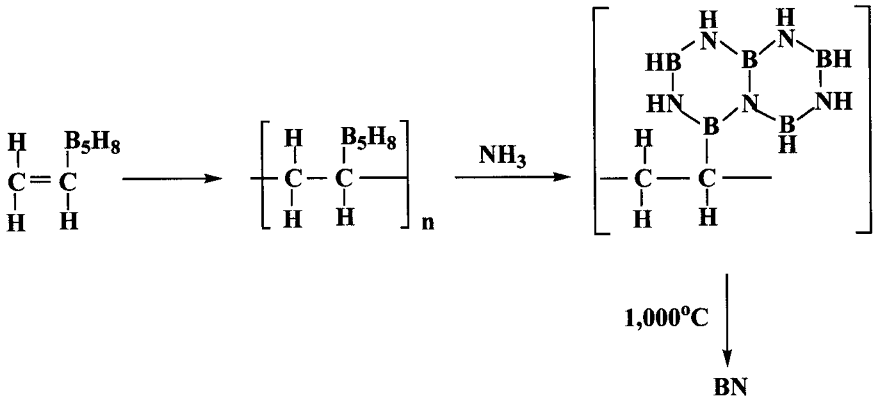
(17)

Unfortunately, borazine itself is quite volatile and any thermolysis reactions must be conducted in a pressure vessel with provision for removal of hydrogen as the pyrolysis proceeds.

A decrease in volatility can be achieved by the linkage of borazine rings to form a cyclolinear oligomer or polymer of the type shown in **9.19**. Oligomers that approximate to this structure have been produced by the controlled dehydrogenolysis of borazine (reaction (15)) and these yield *t*-boron nitride when heated to 1,000 °C.[55–60]

Other approaches to boron nitride, by Paine, Paciorek, and Sneddon and their coworkers are shown in reaction sequences (16) and (17), processes that involve the loss of Me_3Si, NH_2, or Cl side units from borazine rings as pyrolysis proceeds in the temperature program leading up to 1,000 °C.[61–63]

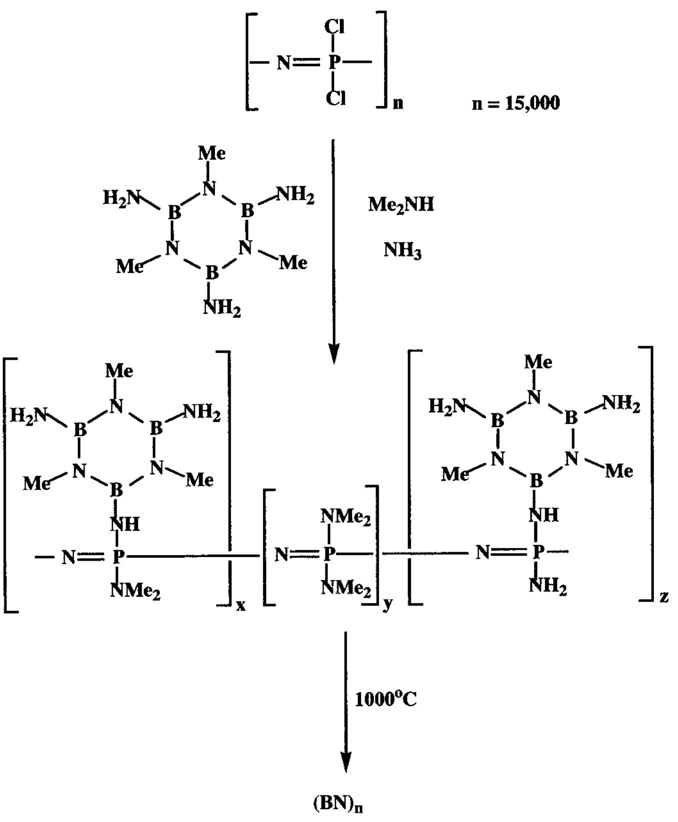
A sacrificial carrier polymer approach was reported by Sneddon in 1988.[64] Here, an organic polymer with a pentaborane side group was prepared by addition polymerization as shown in reaction (18). Treatment of this polymer with ammonia converted the borane side group to a fused borazine (naphthalene-type) side unit. Subsequent pyrolysis in ammonia resulted in loss of the organic polymer and hydrogen and the formation of boron nitride.



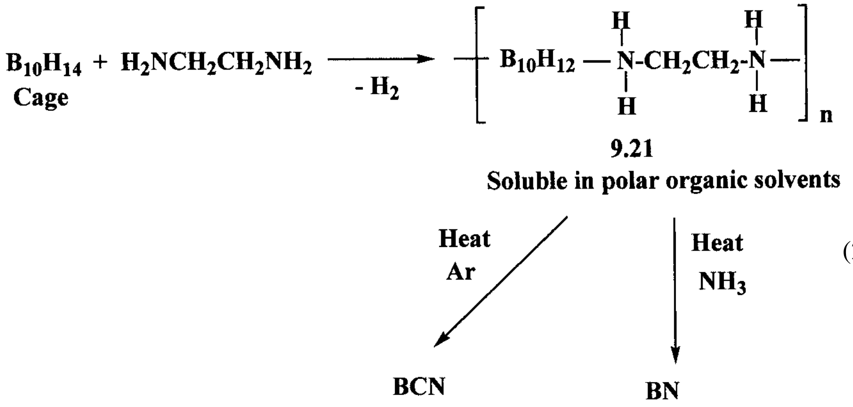
(18)

A related synthetic strategy by Allcock and Welker[65] is illustrated in reaction (19). Here, borazine side groups are linked to a polyphosphazene chain. This reduces the volatility of the borazine and allows facile fabrication of the linear high polymer. Subsequent pyrolysis at temperatures up to 1,000 °C results in breakdown of the phosphazene carrier backbone (possibly via the formation of volatile phosphorus nitride) and formation of boron nitride.

The third approach, this one by Seyferth, is based on the coordinative linkage of borane cage structures by diamines or phosphines to form soluble oligomers (**9.21**), followed by pyrolysis (reaction (20)).[66–68] Pyrolysis in an inert atmosphere gives a 70–90% ceramic yield of a black boron carbonitride, but pyrolysis in ammonia yields white BN in 70% yield. A disadvantage of a process based on a borane starting material is its high cost.



(19)



(20)

9.7 Boron Carbide (B_4C)

A preceramic, carrier polymer route to boron carbide has been reported via the pyrolysis of a polynorbornene that bears decaborane side groups.[69] An important feature of this development is the ability to produce nanofibers of boron carbide in the following way. A solution of the poly(norbornenyldecaborane) in THF is subjected to the process of

electrostatic-spinning in which the solution is extruded from a syringe and caused, by means of a high voltage electric field, to stretch into nanofibers. These deposit on a target electrode as a mat of fibers which are then pyrolyzed at temperatures up to 1,300 °C to yield boron carbide micro- and nano-fibers. Ceramic fiber mats of this type may be useful for the reinforcement of other high temperature materials.

9.8 Aluminum Nitride (AlN)

Aluminum nitride is one of the few materials that is both a good thermal conductor and a good electrical insulator. It is also a high-temperature ceramic, that has a low thermal expansion coefficient, and a low dielectric constant. It is also stable to molten metals such as aluminum, has good wear resistance, and good thermal shock resistance.

Various preceramic oligomer and polymer routes to aluminum nitride have been investigated.[70] For example, the reaction of $LiAlH_4$ or AlH_3 with ammonia initially yields $Al(NH_2)_3$, which loses ammonia and hydrogen during pyrolysis and leaves AlN contaminated by carbon from the initial reaction solvent.[71]

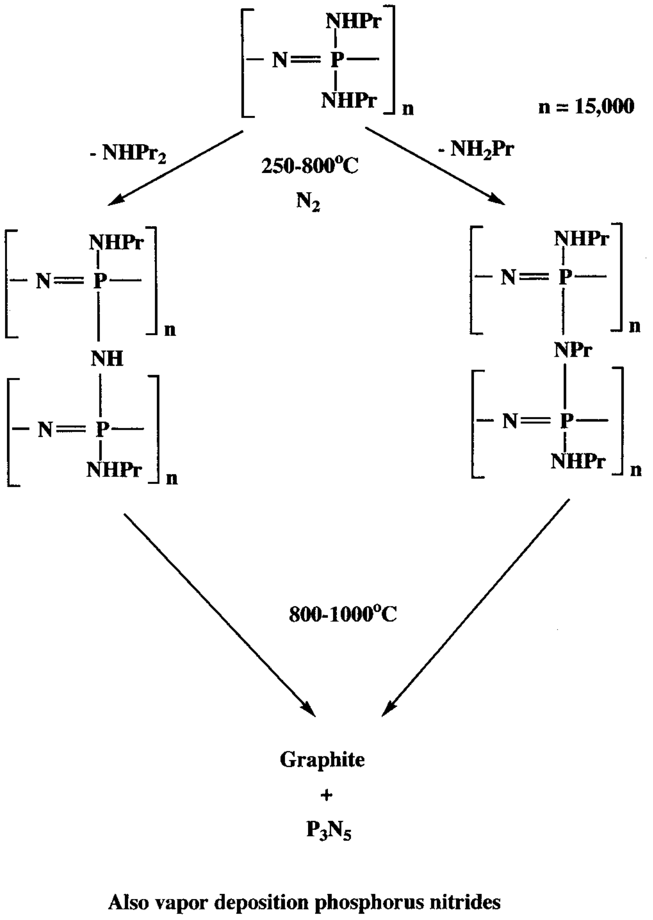
Fibers of aluminum nitride have been produced by the melt-spinning of ethylalazanes derived from the reactions of triethylaluminum and ammonia.[72] The spinnable products have compositions such as $[(EtAlNH)_x(Et_2AlNH_2)_y(Et_3Al)_z]_n$ which probably consist of linked alazane rings and chain structures. Pyrolysis in ammonia gives aluminum nitride fibers.

Interrante and coworkers reported techniques for the preparation of alloys of SiC and AlN by the copyrolysis of precursors to both silicon carbide and aluminum nitride.[73,74] The source of the aluminum component was commercially available aluminum alkyls, AlR_3 (R = Me, Et, or *i*-Bu) which, when treated with ammonia, initially give cyclic alazanes such as $(R_2AlNH_2)_x$, and cross-linked species RAlNH by pyrolytic loss of RH. Further pyrolysis gives a high purity, oxygen- and carbon-free AlN in nearly quantitative yield.[73,74] The iso-butyl derivatives are preferred for this reaction because higher temperature reactions are allowed, and this permits copyrolysis with the poly(carbosilane) silicon carbide precursor. Copyrolysis took place initially at 170 °C, but later at temperatures up to 350 °C under nitrogen, and then up to 2,000 °C to give a homogeneous SiC/AlN ceramic.

9.9 Phosphorus Nitride (P_3N_5)

Although phosphorus nitride is not a high-temperature ceramic, it can be prepared by the pyrolysis of polymers, in this case polyphosphazenes. Polyphosphazenes that bear aliphatic amino side groups lose amines and are cross-linked during pyrolysis in nitrogen at 250–800 °C, and then decompose to a mixture of graphite and phosphorus nitride, P_3N_5, between 800–1000 °C.[75] The chemistry is summarized in reaction (21). A form of phosphorus nitride sublimes from the mixture at the highest temperatures.

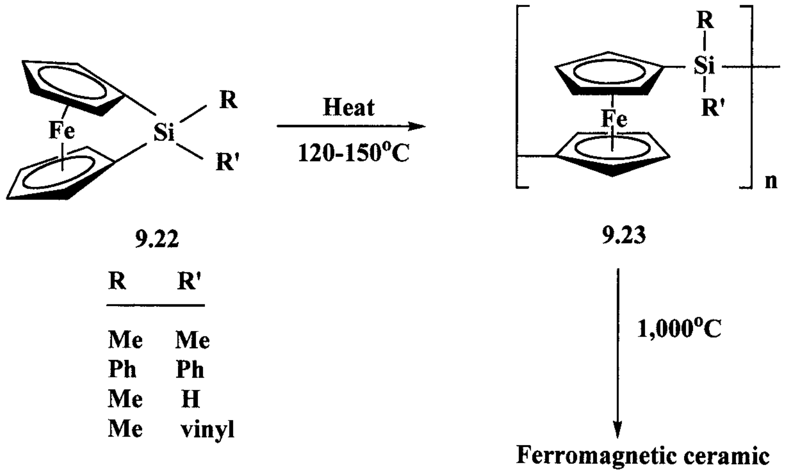
It is also known that cyclic trimeric aminophosphazenes undergo similar reactions when heated to give linked ring systems called "phospham". Presumably this is another potential intermediate en route to phosphorus nitride.



(21)

9.10 Poly(ferrocenylsilanes) as Ceramic Precursors

Manners and coworkers described the formation of ferromagnetic ceramic materials by the pyrolysis of poly(ferrocenylsilanes) with the structure shown in **9.23**.[76] The polymers are prepared by the thermal polymerization of the ferrocenylsilanes (**9.22**) shown in reaction (22). Pyrolysis of the polymer under nitrogen proceeds in steps. The polymer is stable to weight loss up to 250 °C, but loses ferrocene, the original monomer, and a cyclic dimer during the heating program up to 1,000 °C. The final ceramic is a black, lustrous material that is attracted to a bar magnet. Its composition is 11% iron, 17% silicon, and 58% carbon, with the carbon being concentrated at the surface. The α-iron sites are smaller than 30 nm. The highest yields of the ceramic are achieved when the side groups attached to silicon are hydrogen or vinyl, presumably because these units facilitate cross-linking during the initial heating process.



(22)

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